



PHD

The importance of hydrodynamics and mechanical action in fabric washing

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The Importance of Hydrodynamics and Mechanical Action in Fabric Washing

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A thesis submitted for the degree of Doctor of Philosophy

University of Bath

Department of Chemical Engineering

March 2017

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Abstract

Washing fabrics is a ubiquitous process that has been found to have been common even in early civilisations. The process can be performed by hand or with the aid of a washing machine, giving rise to a wide range of wash conditions. Although this process is very common the mechanisms involved are poorly understood, but are thought to involve chemical, mechanical and hydrodynamic inputs. The main aim of this project is to test whether these inputs can be used to improve the efficiency of cleaning fabrics at lower temperatures, and to better understand the mechanisms involved in these individual actions.

The cleaning of polyester and cotton fabrics soiled with artificial sebum has been investigated with 20 °C, 40 °C and 60 °C wash solutions. Fabrics have been cleaned with a model surfactant system consisting of Linear Alkylbenzene Sulfonate (LAS) at 0.1 times and twice the Critical Micelle Concentration (CMC), and results compared to water. Bespoke rigs to simulate rubbing, stretching and flow have been optimised and methods developed for cleaning and analysis of fabrics. Cleaning has been characterised by mass change, colour change and resistance change. Mass change gives an indication of the overall removal, whereas colour gives an analytical measure of the difference in the appearance of the fabrics, and change in resistance to flow of water through the fabric shows how much sebum has been removed from the pores. Additional analysis has been completed on the fabrics including FTIR, mass per unit area, SEM and zeta potential measurements.

Removal was highest when the fabric was washed at 60 °C with a high concentration of surfactant. Soaking alone removed some of the mass, but this increased when mechanical action was also used. Of the mechanical actions, rubbing was found to be the most effective under most conditions. On the whole, cleaning was more effective at 40 °C than 20 °C, and a higher concentration of surfactant aided removal of soil to a greater extent than at a lower concentration or with water alone. However, some exceptions to these trends have been identified.

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Nomenclature

Latin

a^* CIE $L^*a^*b^*$ Colour space, red-green axis

A Strip area, m^2

b^* CIE $L^*a^*b^*$ Colour space, blue-yellow axis

C_d Discharge Coefficient

d Gauge tube inner diameter, m

d_t Gauge nozzle throat diameter, m

F Force, N

h_0 Clearance of gauging nozzle from substrate, m

h Clearance of gauging nozzle from a surface, m

J Flux, $m.s^{-1}$

k conductivity, $\mu S.cm^{-1}$

L Length, m

L^* CIE $L^*a^*b^*$ Colour space, black-white axis

m Mass, g

M Molar concentration, $mol.L^{-1}$

m_g Gauging mass flow rate, $kg.s^{-1}$

p	Pressure, Pa
Q	Volumetric flow rate, $\text{m}^3.\text{s}^{-1}$
Re	Reynold's Number
R_m	Resistance, m^{-1}
s	nozzle rim width, m
t	Time, s
T	Temperature, $^{\circ}\text{C}$
$\%T$	Percentage transmission, %
u	Velocity, $\text{m}.\text{s}^{-1}$
V	Volume, m^3

Greek

α	FDG nozzle angle
γ	Surface tension, $\text{N}.\text{m}^{-1}$
Δp_{ij}	Pressure drop between points i and j , Pa
δ	Deposit thickness, m
ζ	Zeta potential, mV
θ	Contact angle, $^{\circ}$
κ	Permeability, m^2

μ Fluid viscosity, Pa.s

ρ Density, kg.m⁻³

Abbreviations

AFM Atomic Force Microscopy

CFD Computational Fluid Dynamics

CMC Critical Micelle Concentration

DAQ Data Acquisition

DSC Differential Scanning Calorimetry

FDG Fluid Dynamic Gauge

FTIR Fourier Transform Infra-Red

LAS Linear Alkylbenzene Sulfonate

LCA Life Cycle Analysis

MEA Monoethanolamine

MPG Mono Propylene Glycol

NI Non-ionic

RO Reverse Osmosis

SEM Scanning Electron Microscopy

SRI Stain Removal Index

TEA Triethanolamine

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Chapter 1: Introduction

1.1. Context

The washing of fabrics, whether by hand or washing machine, is a common process. Globally, it is estimated that 300 billion fabric washing operations occur annually (Muir et al., 2013). The process of washing fabrics uses large amount of energy, water and chemicals. The combination of this and the frequency of fabric washing operations makes it an important environmental issue.

The interactions of mechanisms involved in fabric cleaning are poorly understood, but include mechanical actions, chemical actions and hydrodynamics, with temperature and time also having key effects. This is summarised in Figure 1.1 below. Factors investigated in this thesis are shown in black.

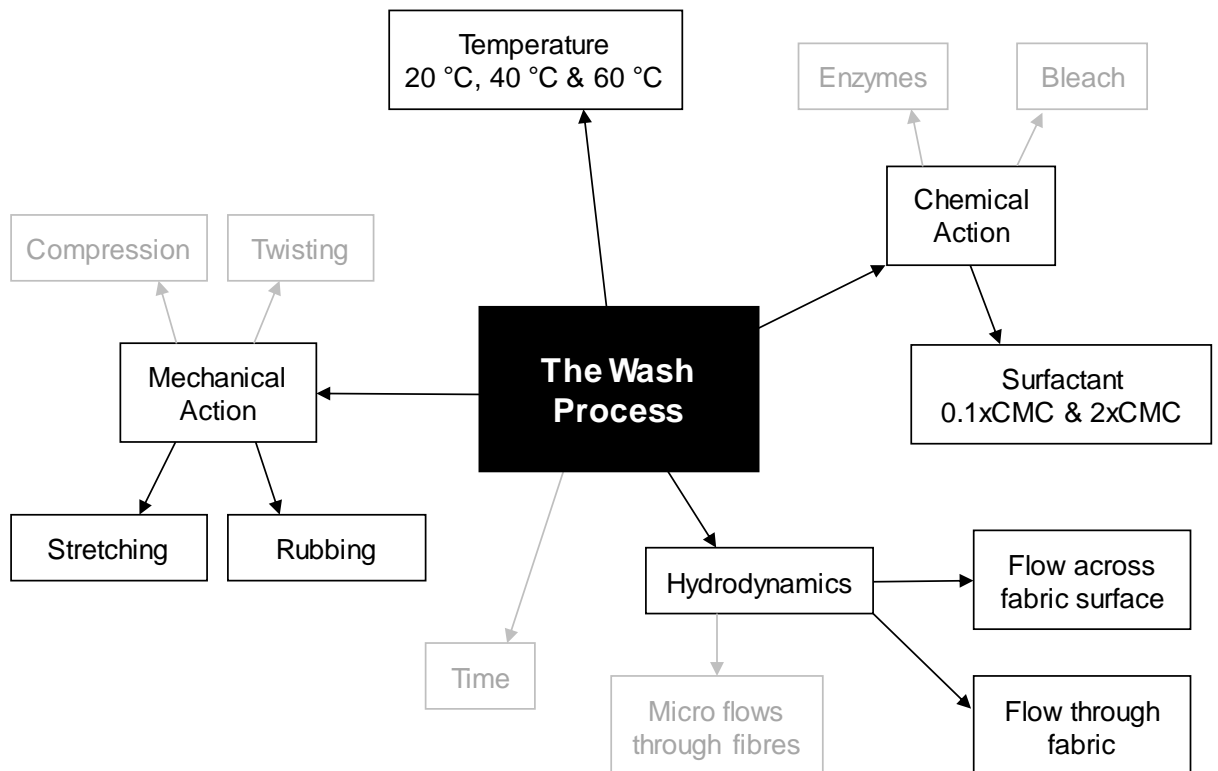


Figure 1.1. Factors involved in the cleaning of fabrics. Those in black will be investigated in this thesis.

100% polyester and 100% cotton fabrics have been used in testing to investigate fabric cleaning, allowing insight into the differences in cleaning between different fabric types. Sebum, a mixture of organic compounds produced by the body, was chosen as the soil since it presents a difficult cleaning problem, especially in developing and emerging markets. To simplify the process and create a model system a single surfactant, linear alkylbenzene sulfonate (LAS), was selected for testing. Fabrics have been washed at two surfactant concentrations, 0.1 x CMC and 2 x CMC, as well as with water, at three different temperatures, 20 °C, 40 °C and 60 °C. Bespoke equipment has been constructed to individually examine the effects of stretching, rubbing and flow of water to improve the mechanistic understanding of the wash process.

1.2. Structure of Thesis

This thesis is divided into nine chapters. Brief descriptions of the scope of each chapter are given below.

Chapter 1 gives a general introduction to the research and outlines the aims and objectives of this research, as well as providing a list of dissemination of research.

Chapter 2 presents a review of the current and historical literature and scientific theory from relevant areas of investigations with fabric, as well as work done with other porous materials. This provides the context for this research.

Chapter 3 details the materials used including fabrics, soils and surfactants, and the experimental methods employed throughout the work. It details the changes made to experimental methods and discusses why these changes were important, as well as discussing the development of a new rig and modifications to existing rigs.

Chapter 4 reports and analyses the properties of the chosen fabrics, soils and surfactant.

Chapter 5 examines the chemical action involved in fabric cleaning without mechanical action or hydrodynamics, allowing comparison with the work presented in later chapters.

Chapters 6, 7 and 8 investigate and report on the findings of experiments with optimised methods and equipment to investigate the individual factors involved in fabric cleaning. Chapter 6 focuses on hydrodynamics and chapter 7 on mechanical actions. Chapter 8 compares each of the individual actions.

Chapter 9 concludes the results presented in chapters four to seven, and presents ideas for future study using the bespoke equipment to investigate cleaning of fabrics.

1.3 Aims and Objectives

The main aim of the project was to test whether chemical action, hydrodynamics and mechanical actions can be used to improve efficiency of cleaning when lower temperatures are used. To do this, bespoke rigs were used to decouple the mechanisms involved in the washing process allowing investigation of hydrodynamics, mechanical and chemical actions individually. In order to achieve this aim, the research objectives were:

- i) Optimisation of bespoke equipment and analysis methods to ensure they are fit for purpose.
- ii) Investigation into whether hydrodynamics and mechanical action can be synergistically assembled with chemical inputs to compensate for the loss of thermal energy in low temperature fabric washing.
- iii) Use of Fluid dynamic gauging, a tool used to determine the strength of soil layers on fabrics, to give a better understanding of the soil layer itself and its behaviour during cleaning operations.
- iv) Investigation into the difference in cleaning between different fabrics, polyester and cotton, with an oily soil.

- v) Investigation into mechanisms of removal above and below the CMC. If a sudden step change is observed in cleaning efficiency when the CMC is reached this would indicate other mechanisms, in addition to roll up, become active in the cleaning process.

The flow rig was used to simulate hydrodynamic effects, and the stretching and rubbing rigs were used to simulate mechanical effects. All three rigs were used to investigate the effect of surfactant on cleaning at a high level, twice the CMC of the surfactant, and low level, 0.1 times the CMC of the surfactant. Experiments have been completed with the full range of wash solutions at 20 °C and 40 °C, as well as at twice the CMC of the surfactant at 60 °C to give the best possible cleaning.

1.4. Dissemination of Research

1.4.1. Conference Presentations

The work in this thesis was presented at the following conferences and workshops:

2nd Annual InterPore UK Chapter Meeting, University of Loughborough, UK, September 2016.

Oral Presentation.

First WIRC Water Science and Engineering Conference, University of Bath, UK, July 2016. **Poster Presentation.**

ACS 20th Annual Green Chemistry & Engineering Conference, Portland, Oregon, June 2016. **Poster Presentation.**

ChemEngDay UK, University of Bath, UK, March 2016. **Oral Presentation and Poster Presentation.**

FDG Workshop, University of Cambridge, UK, December 2015. **Oral Presentation**

FDG Workshop, Braunschweig University of Technology, Germany, December 2014. **Oral Presentation**

1.4.2. Awards

Travel Grant for ACS 20th Annual Green Chemistry & Engineering Conference. £150 towards travel to this conference from the IChemE Water Special Interest Group.

Best Second Year Seminar Presentation – Department of Chemical Engineering, University of Bath. £500 towards conference attendance in my final year.

Runner Up Prize for Water Technology Poster - ChemEngDay UK, University of Bath. £25 from the IChemE Water Special Interest Group.

Chapter 2: Literature Review

This chapter gives an introduction to the issues surrounding fabric cleaning, and the vast range of wash conditions used by consumers. It reviews current and historical literature on fabrics, chemicals used in laundry detergents, and common and problematic soils, and outlines various mechanisms of cleaning reported. It also includes details on analytical techniques already used to study fabrics cleaned in the laboratory, as well as potential techniques that could be used, some of which have been employed later in this thesis.

2.1. Laundry and Sustainability

According to the World Commission on Environment and Development (1987), “Sustainable development is development that meets the needs of the present without compromising the ability of future generations to meet their own needs”. Seuring et al. (2003) considered it to have three dimensions: environmental, economic and social. In the context of fabric washing, the environmental dimension includes both consumption of resources and negative impacts on the environment (DEFRA, 2009). The economic dimension is linked to the fact that the more environmentally friendly option cannot be more costly for the consumer. The social dimension involves changing consumer habits in terms of wash temperature and detergent dosage. This work will focus on the environmental dimension.

According to DEFRA (2009), it is difficult to estimate the exact environmental impact of the wash process as there are many variables including frequency of washing, wash temperatures, method of drying and detergent used among others, however Bajpai and Tyagi (2007) noted that detergents have a large environmental impact as they are non-renewable (one time use). The use of large volumes of fresh water, from 5 L to 68 L, is significant as it may decrease the amount of water available for drinking (Wertz, 2009). LCA performed by Saouter and Van Hoof (2002) found that 80% of energy consumption of a detergent is during the consumer use phase.

Washing fabrics requires thermal energy, mechanical action and chemical action (Sabaliunas et al., 2006). When time is included, these are collectively known as the Sinner Parameters, as shown in Figure 2.1 (Warmoeskerken et al., 2002). Conservation of one of these requires compensation by the others. Currently consumers can control all four. Sabaliunas et al. (2006) concluded that the greatest energy saving is possible by thermal energy conservation. Laitala, Boks and Klepp (2011) reported the energy used in fabric washing to be 0.370kWh at 30 °C, increasing to 0.526 kWh at 40 °C and 0.895 kWh at 60 °C. This means that washing at 30 °C instead of 60 °C reduces energy consumption by 58.7 %, and a small reduction from 40 °C to 30 °C used 29.6 % less energy.

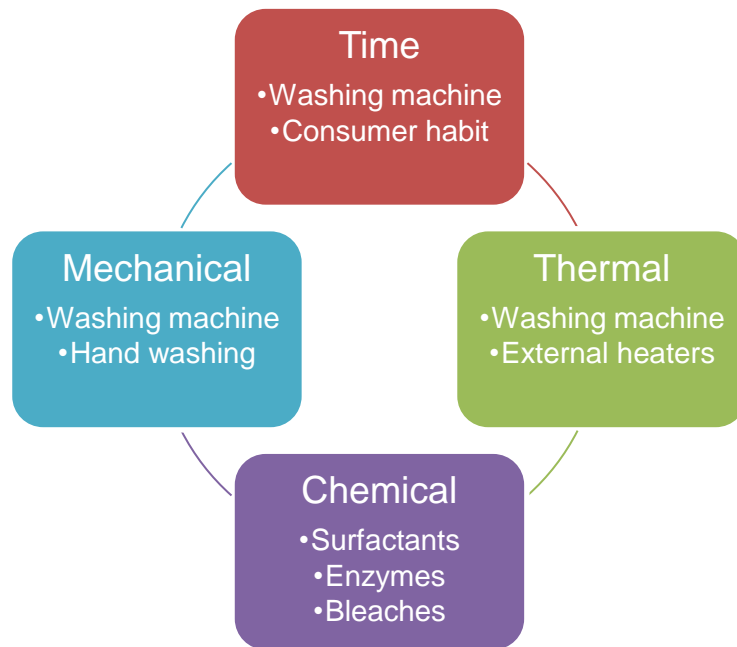


Figure 2.1. Inputs required for cleaning

An ideal wash cycle would include non-toxic chemicals that are effective at lower temperatures, preferably room temperature, and require little mechanical work to avoid damage to fabrics.

2.2. Fabrics

Fabrics are three dimensional porous structures made of yarns, which in turn are made of fibres, as shown in Figure 2.2. Moholkar and Warmoeskerken (2004) found that the majority of flow is between the yarns in the inter-yarn region, as there is less resistance than the path through the yarns

(intra-yarn region). Because of this a fabric can be thought of as a bi-porous material consisting of larger inter-yarn pores and smaller intra-yarn pores. This is most easily observed with weaved fabrics.

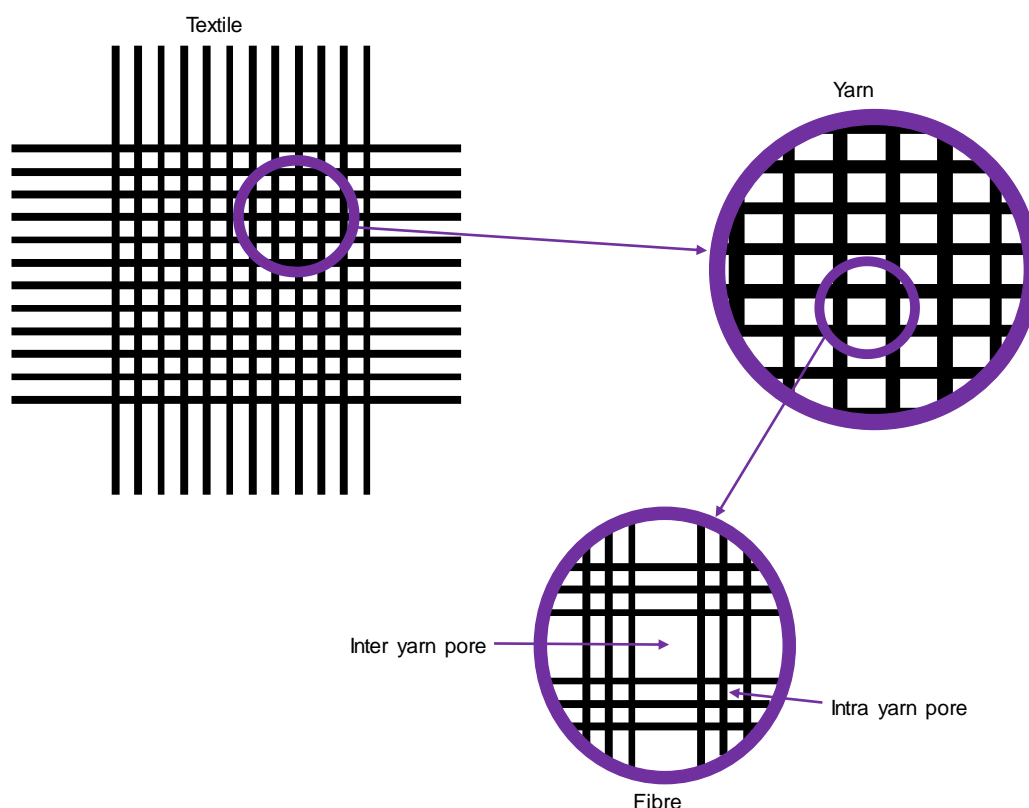


Figure 2.2. Diagram of structure of textiles. Adapted from Moholkar and Warmoeskerken (2004).

As well as weave, the size of these pores is affected by number of yarns per unit area, yarn linear density, yarn diameter, yarn twist, fibre diameter and hairiness (Unal, 2012).

The majority of a common wash load is made of cotton, polyester or fabrics that are a mixture of the two. The wash load may also include silk, wool, linen and nylon. The fabric used in laboratory testing is important as different fabrics have different surface properties such as wettability, hydrophobicity and strength. These properties, as well as density, permeability and weave pattern, will affect soiling of a fabric and ease of cleaning (Wang et al., 2007).

Cotton, after scouring and bleaching, is 99% cellulose. Cellulose is a polymer consisting of linked glucose molecules and polymer chains, which are then held together by hydrogen bonds (Cotton Incorporated, 2016). Polyester fabrics are made from synthetic fibres, which consist of long chain polymers (TEonline, 2016). This makes the fibres both stable and strong. Different synthetic fibres are used to give a range of polyester fabrics with different characteristics. Polyester is made of cylindrical fibres with few or no imperfections. Obendorf (1983) observed no oil within the interior regions of synthetic polyester fibres. Cotton has a more uneven surface and contains many imperfections. These cracks and crevices can trap soils and make cleaning more difficult. Robbins (2012) has observed a similar effect when studying fibres of human hair.

Cotton is highly absorbent due to its hydrophilic nature, and readily absorbs moisture from the air (Masson and Richards, 1906). On the other hand, polyesters are hydrophobic. Hsieh (1995) reported that cotton can retain four times as much water as polyester. However, the wicking properties of polyester can be altered with surfactants, but these will be removed in subsequent washing (Harnett and Mehta, 1984).

As well as differences arising from the different materials, the weave pattern of the fabrics also has a significant effect on flow through the fabric, which in turn has an effect on cleaning (Lu and Tung, 1996). When woven fabrics are considered, plain weave gives the highest fluid flow resistance.

Previous work by Bowers and Chantrey (1969) comparing cotton and polyester fouled with sebum showed that they absorb similar amounts of oily sebum from the body, but polyesters are harder to clean as they do not wet as easily as cotton. The wettability of a fabric can affect the cleaning as the higher wettability of the fabric, the more surfactant comes into contact with the soil by increasing the soil-water interface, hence increasing surfactant penetration (Cox, Smith and Russell, 1987).

Obendorf and Klemash (1982) studied the penetration of triolein, another oily soil, into cotton and polyester fabrics. They found that triolein accumulated in the interfibre capillaries and within the

crevices of fibres for cotton, whereas for polyester triolein was not found in the interior region of the fibre, but residual soil remained on the fibre surface after cleaning.

There are some similarities between fabrics and membranes. Both are porous materials that can be soiled, although in different ways, and require subsequent cleaning by chemical, mechanical or hydrodynamic actions. For that reason some analysis techniques currently used on membranes are evaluated in Section 2.8 based on their suitability for use on fabrics.

2.3. Soils

In this report, the term soil is used to describe the unwanted accumulation of both liquid and particulate materials on the textile, both on the surface and within the fibres, which has an undesirable effect on the appearance of the fabric. A fabric can become soiled in a number of ways; when it comes into contact with another soiled solid, a liquid or from contact with air borne soils (Venkatesh et al., 1974). According to Visser (1988), soil adheres to a surface due to van der Waals forces, electrostatic forces, contact area or surface reactions, or combinations of these.

Soils are commonly coloured, and are often localized (Bajpai and Tyagi, 2007). They come from the body of the wearer or from the environment, and soils found on clothing garments are generally a mixture of fluid and solid particles (Chi and Obendorf, 1998). These are better known as particulate soils, which retain their geometry when in contact with a fabric surface, and oily soils, which tend to wet the fabric, as shown in Figure 2.3. The fluid is often oil or grease, such as oil from automobiles and machinery, secretions from the human skin or oils from foods. Examples of solid components include clay minerals, sand, rust or soil.

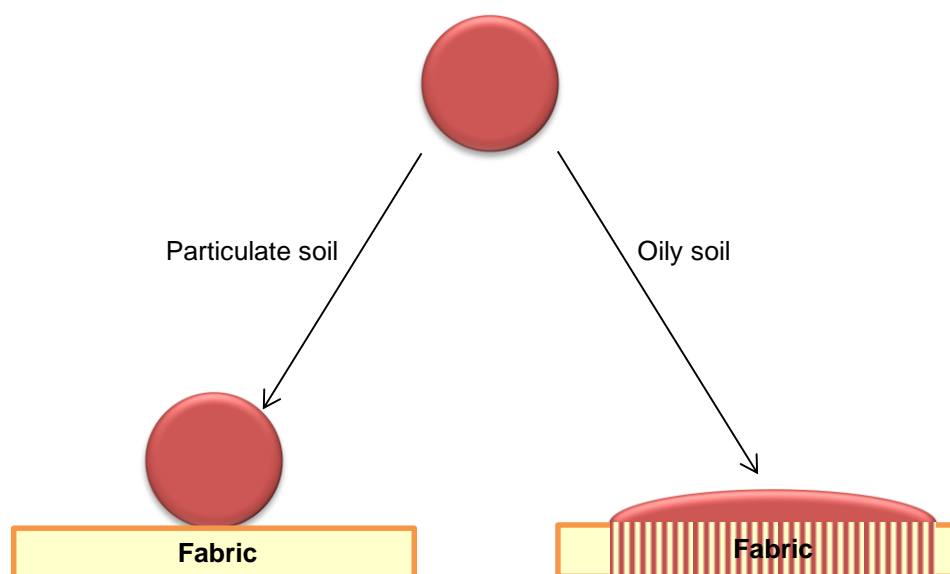


Figure 2.3. Behaviour of particulate and oily soils on fabric surface

Studies have shown that the oily soils create a coating on the fibre, and particulates are embedded within this layer. In the absence of oily soils, particulate soils most often attach by adhesion, and not by mechanical entrapment (Kissa, 1973). Adhesion will be stronger with increased pressure and mechanical work applied during the soiling procedure. For particulate soiling, fabric geometry is more important than chemical composition of the surface.

Soils are not the same as stains (Kissa et al., 1991). The term stain can refer to either the substance that causes the stain or the resulting discolouration on the fabric surface. Molecules of a coloured substance deposit on or in fibres causing a stain. A stain can also be caused by molecules of residual soil. Stains are seen to be more permanent than soils, and include synthetic food colours, blood, and oxidation products of residual soils. A bleaching agent or enzyme is often required to remove stains.

As well as the type of soil, the quantity of soil, its structure, and its age will all affect the cleaning (Bird, 1993). Utermohlen and Wallace (1947) found that soiled fabrics became more difficult to wash after storage for a number of weeks or months. They reported that the only way to avoid this was to store samples in a dry and inert atmosphere.

2.3.1. Sebum

Sebum was the main soil used in this body of work. It is a mixture of organic compounds produced by the sebaceous glands, which coats the human skin surface and hair to provide lubrication and waterproofing. Sebum is odorless, but when broken down by bacteria can produce odors (Draelos, 2004). Weglinski and Obendorf (1985) report that the adsorption of sebum by clothing often is 1 to 2 % of the weight of the garment. This lipid mixture is comprised of fatty acids, squalene, wax monoesters, cholesterol esters and triglycerides (Camera et al., 2010). The composition of the artificial sebum used in this work can be found in Section 3.1.2. Breuer (1981) noted that the amount and composition of sebum secreted by the sebaceous glands varies with age, sex, the season or time of the year, and nutrition. As noted by Wertz (2009) and Park and Obendorf (1994), after secretion the chemical and physical properties of sebum can change with time, particularly since more than half of the constituents are unsaturated and therefore more reactive.

Sebum is thought to create a layer around a fibre in the fabric, which then aids adherence of otherwise loosely adhered particulate soils to the surface (Utermohlen et al., 1949). In developing and emerging countries in particular, incomplete removal of sebum and subsequent build up can aid fouling by particulate soils.

Surfactants have been found to selectively remove particular constituents of sebum, and polar materials are more easily removed than non-polar materials such as waxes. Clarke, Clarence and Robbins (1989) noted that triglycerides are the most readily removed from hair and Clarke, Robbins and Schroff (1990) reported that ester and paraffin wax were the most difficult to remove, while the order of removal of other constituents varied with temperature. It was also found that both surfactants investigated showed greater selectivity for removal of components at higher temperatures, which may be linked to the individual melting points of the constituents.

2.3.2. Lard

Lard was used for some preliminary testing, but it was decided that sebum was a more common and problematic soil and therefore was used for the majority of testing. Lard is an animal fat primarily composed of mixed triglycerides of palmitic, oleic and stearic acids (Powe, 1963). It has been found that lard is more difficult to remove than sebum, which is thought to be due to the size and shape of the molecules, melting point, and polarity of the material. Varanasi et al. (2001) found that when lard is used to soil fabrics, the samples have large deposits on the surface, whereas sebum is distributed more evenly throughout the textile.

2.4 Chemical action

In the wash process, the chemical action is a result of the detergent used. Jennings (1965) defined a detergent as any substance that could aid removal of soil. In the context of washing fabrics, a detergent is a mixture of chemicals used to remove an unwanted substance (soil) from a solid surface, but they often have other functions such as reduction of water hardness (DEFRA, 2009). To be effective, a detergent also needs to prevent redeposition of the soil, so the soil has to be suspended in the solution after removal (Trost, 1963). Detergents primarily consist of surfactants, and can also include enzymes, bleaches, builders and auxiliary compounds, each detailed individually below (Jurado, 2006). Requirements of modern detergents include long term stability of components during storage, appropriate short-term functionality, action at low temperatures, reasonable cost and minimal environmental impact.

2.4.1. History

The oldest reference to soap dates back to 2200 BC, which consisted of water, alkali and cassia oil. The process of making soap involves boiling fats or oils with alkali, a process which continued as the main method of manufacturing detergents until World War 1. However, as noted by Kosswig (1994) and Effendy and Mailback (2006), the development of surfactants was required to support the

growing textile industry, with the added pressure of soap shortages in Germany during World War 1. Research into synthetic detergents began at this time, but the first commercially viable surfactants were not developed until the 1930s (Smulders et al., 2007). Enzymes for use in laundry detergent were first investigated in the early 20th century, but were not introduced until much later due to thermal stability issues (Roald, 1969). They are now a key ingredient in laundry formulations. Builders were introduced in the United States in 1947, beginning with sodium diphosphate (Bajpai and Tyagi, 2007). A change was seen in the 1960's due to increased environmental awareness; which included the removal of phosphates from detergents, causing issues for stain removal (Kosswig, 1994).

2.4.2. Forms of detergent

Traditionally, laundry detergent is found in powder form, however liquid detergents are growing in popularity and may even exceed the use of solid detergent (Bajpai and Tyagi, 2007). LCA data suggests that compact powders and concentrated liquids are more environmentally friendly than regular liquids and powders (DEFRA, 2009). This is due to the reduction in size and weight leading to lower transportation requirements and less storage space and packaging, and the lower use of chemicals per wash.

Liquids generally contain higher levels of surfactant, often up to 50 % compared to only 25 % in powders. Liquids can be found in two forms, gel or HDL (heavy duty liquid). Gels provide a better detergency performance but there are often stability issues. There is also now the option to use a unit dose product, which can be a powder or liquid.

2.4.3. Surfactants

Surfactants are organic compounds containing both a polar, hydrophilic head group (either charged or uncharged) and non-polar, hydrophobic tail, giving them surface-active properties, as shown in Figure 2.4. The hydrophobic portion of the molecule will often consist of long chain fatty acids,

alcohols or alkylbenzene groups, and the hydrophilic portion can consist of sulfates, carboxylates and quaternary ammonium salts, among others. This allows water insoluble materials to be solubilised, therefore making surfactants ideal cleaning agents (Racaud, Serrano and Savall, 2010). Surfactants work by lowering the surface tension at the fabric-water and soil-water interfaces, whilst increasing repulsion between the fabric surface and soil (Olsen and Falholt, 1998). Surfactant properties such as wetting ability, emulsifying ability and foaming can be controlled by altering the chemistry of either the hydrophobic or hydrophilic group of the surfactant.

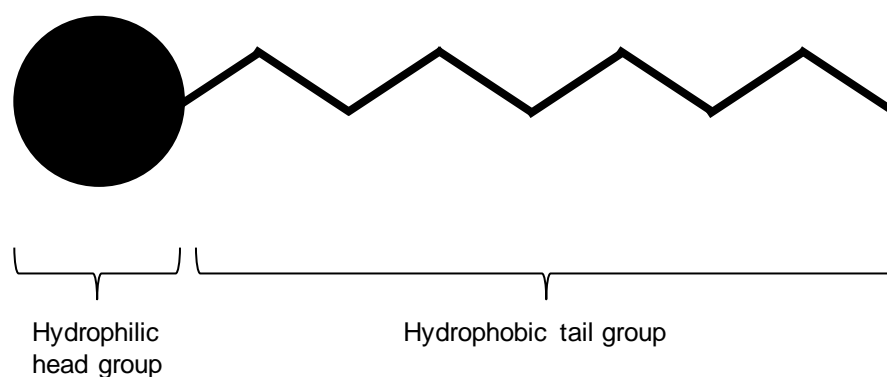


Figure 2.4. Schematic of surfactant molecule.

Synthetic surfactants are widely used in detergents and textiles, but can also be used for oil recovery, pesticide formulations and polymers. In 1998 the global production of synthetic surfactants was estimated to be 7.2 million tons annually (Ying, 2006).

Of great importance to the use of surfactants in detergents is the critical micelle concentration, or CMC. The CMC refers to the concentration below which surfactants exist as individual molecules, and above which micelles form. Micelles are clusters of surfactant molecules with the hydrophobic tails oriented towards the interior of the micelles and hydrophilic head group in contact with the solvent, and form to reduce the system's free energy (Ying, 2006). The value of the CMC depends on the surfactant in question, temperature, and presence of strong electrolytes (Racaud, Serrano and Savall, 2010). The CMC is of interest when considering detergency as some mechanisms of cleaning are only possible above this value (Espig, 1997).

The CMC can be found by measuring a suitable physical property of the surfactant and plotting this against surfactant concentration (Dominguez et al., 1997). An abrupt change in the slope of the graph indicates the CMC.

Anionic surfactants

Anionic surfactants are negatively charged and are often found with small cations such as sodium or potassium; however these counter ions have very little effect on the properties of the surfactant (Kosswig, 1994). This class of surfactant is the most popular, representing 53% of all surfactant use, which is largely due to their ease and low cost to manufacture (Yangxin, Jin and Bayly, 2008). Anionic surfactants with 12 to 16 carbon atoms in their hydrophobic chain provide the best detergency. Common hydrophilic groups include carboxylates, sulfates and sulfonates (Bajpai and Tyagi, 2007).

The most common surfactant used in laundry detergent is linear alkylbenzene sulfonates (LAS), which is an anionic surfactant with the general structure shown in Figure 2.5. Originally, branched alkyl benzene sulfonates (ABS) were used in laundry detergents, but it was found that they were more difficult to break down and caused a layer of foam to develop in rivers. LAS, on the other hand, are biodegradable. LAS is sold as a mixture of the homologous series of chain lengths varying from 10 to 14, with an average length of 12. As 12 is the average, LAS can also be known as sodium dodecylbenzenesulfonate. This series of compounds accounts for 40 % of all surfactants used in detergents (Scott and Jones, 2000).

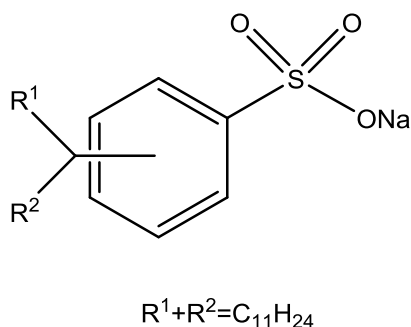


Figure 2.5. Structure of LAS

It has been found that combining surfactants, for example LAS and a linear alcohol non-ionic, affects the CMC, water hardness sensitivity, surface tension and detergency performance. Cox, Borys and Matson (1985) note that the non-ionic acts as a micelle promotion agent and enhances hard water performance, while LAS is still responsible for the surface and interfacial properties. However it is difficult to find an optimally performing mixture as performance is related to temperature, water hardness and cloth type. There are also disadvantages with mixed surfactant systems, for example instability, increased complexity of processing, and raw material costs (Matson and Cox, 1984).

Amphoteric surfactants

Amphoteric surfactants contain positive and negative groups. At their isoelectric point they behave in a similar manner to non-ionic surfactants, whereas above or below this point they show anionic or cationic properties.

2.4.4. Other constituents

Builders are used to soften the water by removal of calcium and magnesium ions by sequestration, precipitation or ion exchange. This is required as surfactant performance is greatly affected by the presence of these hard water ions. Builders also prevent soil redeposition, provide buffering capacity and inhibit corrosion (Olsen and Falholt, 1998). Phosphates were commonly used as builders in detergents, however this led to issues of eutrophication, and therefore zeolites are now replacing phosphates (Kroes, 1980).

Bleaching agents are chemicals that induce a change towards a lighter colour, and those used laundry detergents are often oxidizers such as sodium perborate. Bleach activators may also be added to enhance the performance of the bleach (Smulders et al. 2007).

Enzymes are included in most detergents and aid the breakdown of complex soils. A specific soil requires a specific enzyme, for example protease for proteins or amylase for carbohydrates. Enzymes provide an environmental benefit by achieving the same level of cleaning with shorter wash times,

reduced water consumption and lower temperatures, along with the added benefits of proving fabric care and lowering the pH of the wash solution (Olsen and Falholt, 1998). However, enzymes can be expensive, and incorporating them into a detergent formulation can also be costly (Trägårdh, 1989).

Laundry detergents often contain Monoethanolamine (MEA) or Triethanolamine (TEA). MEA is used primarily for buffering or preparation of emulsions by solubilising other ingredients (Science in a box, 2014), whereas (TEA) is used as a neutralising agent for LAS, resulting in an organic salt that is more soluble in water (Oxiten, 2014). Mono Propylene Glycol (MPG) or Propane-1,2-diol is also commonly used as a hydrotrope, to aid solubilisation of hydrophobic compounds in aqueous solutions. Hydrotropes work by lowering the cloud point of the detergent solution (Aboul-Kassim and Simoneit, 1993). The cloud point is the temperature above which the solution becomes turbid, and prolonged exposure to temperatures above this point can lead to phase separation and instability.

Detergents can contain other components, for example dye transfer inhibitors, corrosion inhibitors, and additives to modify the foaming properties of the solution. Other additives are used to improve the perception of the detergent or the item to be cleaned such as perfumes, optical brighteners and fabric softeners. These components are deliberately deposited on the surface of the fabric during the wash process, and although they are foreign to the fabric they are not considered to be soils (Carroll, 1993). Another common addition to detergents is bacteriostats, which are required as consumers move towards washing at lower temperatures, to prevent the growth of bacteria on fabrics (Aboul-Kassim and Simoneit, 1993).

2.5. Mechanical action and hydrodynamics

The use of mechanical action to aid fabric washing is a well-established practice. Mechanical actions could include rubbing, stretching, beating the fabric by hand, and mechanical action in the washing machine. The amount of mechanical work required is dependent on the forces holding the soil

particles to the fabric, and the strength of the detergent. It would be desirable to reduce the mechanical action required as it can be destructive for the fabrics (Bacon and Smith, 1948).

Lee et al. (2008) developed a piece of equipment to simulate the wash process including hydrodynamic flow, flexing and abrasion. This equipment consists on a tank containing grips to hold a fabric in place as well as to stretch it and rub it, and shake the solution. The speed of shaking and temperature could be controlled. Four soils were tested; red wine, pig's blood, carbon black with mineral oil and a chocolate and milk mixture. Cleaning was then characterised by reflectance measurement using a colorimeter. The benefits of this equipment is it appears to be fairly high throughput and will have a consistent ratio of fabric to water to wash solution, however limitations of this equipment include that removal is only characterised by reflectance change, and it does not give mechanistic understanding as forces cannot be quantified.

The equipment used in this work was developed and initial experiments were carried out by Muir et al. (2013), and separated out flow, rubbing and stretching. Cotton fabric soiled with lard (Sainsbury's basics) that had been dyed with Oil Red O was studied, with Croda's synperonic A7L surfactant, a non-ionic ethoxylated C12-C15 alcohol, as the detergent.

Soaking

During washing, soaking in detergent solution helps to loosen soil on the fabric by mechanisms outlined in Section 2.6. Lee et al. (2008) found that some stains, including red wine and pig's blood, could be partially removed by soaking alone without additional mechanical action, whereas the chocolate milk mixture and carbon black with mineral oil were not removed. Removal of red wine was found to increase quickly over time, followed by a levelling off the washing efficiency. On the other hand, pig's blood removal increased steadily over the 60 minute experiment. This is thought to be due to the mixture of compounds found in blood.

Flow

Experiments performed by Lee et al. (2008) have found that flow alone does not provide sufficient mechanical energy for cleaning. It was found that in some cases negative washing efficiencies were found for some experiments using chocolate soils. This may be explained by the fact that the lightly coloured fats and proteins were removed, leaving behind the darker coloured particulates. Also, soil may have been transferred from within the yarns to the surface of the fabric.

Muir et al. (2013) reported that the action of through flow gave the best cleaning when compared to cross or combined flow. No significant mass was lost at 10 °C under any conditions, and significant removal was only seen at 40 °C. Little difference was seen by increasing concentration of surfactant.

Flexing

Flexing was found to be more effective than hydrodynamic flow (Lee et al. 2008). This is thought to be due to the fact that the detergent solution penetrates the fabric more easily, loosening more soil and allowing transport of the loosened soil to the wash solution. Cleaning increased with time for all soils, however the absolute removal values varied significantly.

Abrasion

Lee et al. (2008) found that abrasion was most effective for all four soils. Values for cleaning peaked after 15 minutes, then washing efficiency was found to decrease with additional time. It is thought to be because abrasive action could break some unstable micelles, causing redeposition of the soil on to the fabrics. All mechanical actions - flow, abrasion and flexing - aided removal of water-insoluble soils to a different extent, whereas water soluble soils could be removed independent of the type of mechanical action applied.

McKeown (2013) found similar results, namely that flexing, abrasion and flow aided cleaning to different extents, and found that temperature had a large effect on removal. Surfactant made little difference to cleaning results for all three actions.

Ultrasound

Warmoeskerken et al. (2002) found that ultrasound may accelerate mass transport in the intra yarn pores in the cleaning process, which is seen to be one of the rate limiting steps. This allows for the use of lower volumes of water and less energy, making ultrasound an option for more environmentally friendly fabric washing. An ultrasound wave causes compression and rarefaction cycles creating voids in the water, causing cavitation and the generation of bubbles. These bubbles can then implode, and when this occurs near the fabric surface they produce jets of liquid towards the fabric surface as well as releasing energy, which together cause the enhanced cleaning action. A benefit of ultrasound is that it has very little damaging effect on the fabrics. Not all studies have produced positive results, Gotoh (2009) found that ultrasound did not increase the detergency compared to traditional stirring, and was in fact found to decrease it in most cases. Gotoh and Hiram (2012) found that cleaning can be uneven and additional soil redeposition was seen compared to shaking a fabric with the same surfactant solution.

McKeown (2013) reported an increase in cleaning when ultrasonication was used as a pre-treatment, when compared to pre-soaking alone, for most surfactant concentrations and temperatures. They concluded that ultrasound pre-treatment either loosens the lard allowing easier removal when flow is then used, or allows removal via a different mechanism.

Microbubbles

Using bubbles during cleaning has been estimated to use up to 70 % less water in American vertical axis washing machines (Hustvedt, 2011). Bansal, Vineyard and Abdelaziz (2011) also claimed that they provide a superior level of cleaning to traditional machine washing.

Thongpiam et al. (2016) reported that the use of microbubbles aided cleaning of fabrics soiled with coconut milk when used as a pretreatment. Cleaning was performed using a Fluid Dynamic Gauge (FDG) to impose shear stress. Average cleaning increased from 72.0% to 95.2% weight removal when the microbubbles pretreatment was used.

2.6. Mechanisms of cleaning

2.6.1. The soiled system

A soiled system consists of three phases (Bird, 1993). Firstly the solid phase, in this case the surface of the fabric. Secondly, an adhesive soil phase, which can be solid or liquid. In work presented here this is the oily sebum. Finally, the liquid phase consisting of the cleaning solution. This creates three interfaces; fabric and soil, soil and cleaning solution and cleaning solution and fabric.

According to Trägårdh (1989), the processes involved in cleaning are:

- (i) Bulk reaction. Some components of the cleaning solution may react in the bulk solution, for example with hard water ions, and therefore are not involved in cleaning.
- (ii) The mass transport of cleaning solution to the surface.
- (iii) The wetting of the soil and/or fabric surface. This depends on relative interfacial tensions.
- (iv) Penetration of cleaning solution into the soil. The cleaning solution can be transported into the soil by capillary forces or molecular diffusion.
- (v) Interaction between the cleaning solution and soil. This includes both physical and physio-chemical changes such as melting, solvation or emulsification, and chemical changes such as hydrolysis or solubilisation.
- (vi) Removal of the soil from the fabric surface by mass transfer. Removal can involve breaking deposit-deposit bonds (cohesive) or deposit-substrate bonds (adhesive) (Chew, 2004).

Steps (ii) and (vi) are dependent on the mass transfer of the cleaning solution, which depends on temperature, flow and concentration. Step (iv) depends on the structure of the soil deposit, and steps (iii) and (v) depend on the properties of the cleaning solution, fabric and soil, and their interactions with each other. According to Chan (1977), steps (iv) and (v) will be the rate limiting steps in concentrated solutions, and step (iii) will be the rate limited step in dilute solutions.

It has been found that the action of the detergent has a significant effect on soil loosening, but has very little effect on soil transfer (Kissa, 1975). In the absence of mechanical action, the soil removed by the detergent causes the local soil concentration around the fabric to increase with time to a saturation point. When this occurs no further soil is loosened from the fabric and cleaning effectively stops.

Removal of soils is the reverse of adhesion and therefore requires energy to remove the soil from the lower energy attached state to the separated state in water. Surfactants reduce the amount of energy required for cleaning via a number of important mechanisms of soil loosening (Bajpai and Tyagi, 2007). Removal can involve one or a combination of the mechanisms discussed below.

2.6.2. Oily soils

Solubilisation

Solubilisation involves dissolving the water insoluble soils in surfactant solution. Soils can be solubilised by incorporation into micelles produced by the surfactant at concentrations above the CMC (Miller and Raney, 1993). These micelles are thermodynamically stable, and retain their hydrophilic shells and hydrophobic core (Chan, Evans and Cussler, 1976). According to Schwartz (1971), solubilisation is the most important mechanism of removal of oily soils from hard surfaces when only small amounts of soil are present, as well as an excess of surfactant. Shaeiwitz et al. (1981) noted that solubilisation rates are often proportional to the concentration of surfactant above the

CMC, and hence proportional to the concentration of micelles. For solubilisation, the important interaction is that of the wash solution with the soil, and the fabric is less important.

For optimum solubilisation, non-ionic surfactants are required to be at a concentration of several times their CMC, and higher still for anionics (Espig, 1997). Also, anionics form globular micelles, as opposed to the more thermodynamically stable rod shaped micelles; therefore for these two reasons solubilisation is not the most important mechanism for anionics.

Roll up

The roll up or roll back mechanism was developed by Adam (1937), and is the dominant mechanism of removal for anionic surfactants. Unlike solubilisation, roll up can occur at surfactant concentrations below the CMC. It occurs as a result of the surfactant aiding wetting of the fabric surface, reducing the soil-surface contact angle from 0° to 180° , which causes oily stains to become spherical and lift off from the surface completely (Kissa, 1981). This occurs as a result of surfactant accumulation at the oil/water interface, as shown in Figure 2.7. Additionally, the detergent must make the fibre surface more hydrophilic to promote roll up (Robbins, 2012). This causes repulsion between the hydrophilic head group and solid fabric surface allowing the oily soil to separate from the fabric surface (Kissa, 1971).

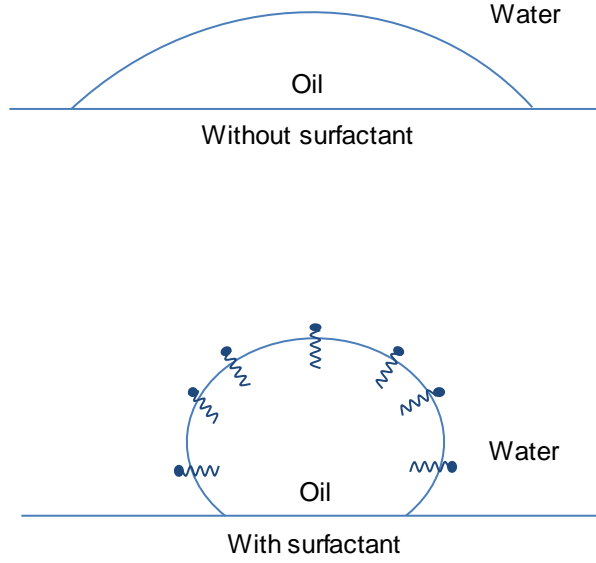


Figure 2.7. Roll up mechanism of cleaning for oily soils.

Roll up occurs when the resultant force of interfacial tensions, f , in Equation 2.1 is positive.

$$f = \gamma_{FO} - \gamma_{FW} + \gamma_{OW} \cos \theta \quad \text{Equation 2.1}$$

where γ_{FO} is interfacial tension between the fibre and oil, γ_{FW} is the interfacial tension between the fibre and water, γ_{OW} is the interfacial tension between the oil and water and θ is the contact angle of the oil on the fibre.

Since $\cos \theta$ can be positive and negative, Equation 2.1 is positive when Equation 2.2 is satisfied.

$$\gamma_{FO} - \gamma_{FW} > \gamma_{OW} \quad \text{Equation 2.2}$$

At wash temperatures above the melting point of the soil, removal is primarily achieved via a roll up mechanism, as the detergent solution preferentially wets the cloth surface (Cox, Smith and Russell, 1987). However, Schwartz (1971) claims that roll up rarely removes all of the soil, especially from rough surfaces. Roll up also depends on the viscosity of the soil, which affects the rate of this process (Kissa, 1981). If the viscosity is too high additional external forces are needed in addition to the interfacial forces to overcome this.

Emulsification

Emulsification, also known as snap-off, reduces the soil-water interfacial tension allowing necking of the soil droplet, causing the outer most part of soil to become incorporated into an emulsion (Sonesson et al., 2007). After absorption of surfactant, if gravitational forces and hydrodynamics become greater than the surface tension forces holding the drop together, this causes the necking effect and draws a droplet away from the horizontal surface (Thompson, 1994 and Kao et al., 1989). If the fabric surface is completely covered in oily soil, the surfactant cannot reach the fibre surface for roll up, so cleaning occurs by emulsification (Dillan, Goddard and McKenzie, 1980). Emulsification can never fully remove an oily soil layer, and will always leave a film with thickness equal to the diameter of the smallest oil droplet (Espig, 1997).

Like roll up, which is possible at any concentration of surfactant, emulsification is possible at concentrations below the CMC. Surfactant molecules stabilize emulsions of oil in water by lowering the oil/water interfacial tension. As such, the oil is able to disperse in the aqueous phase as part of a surfactant aggregate or micelle. This also inhibits redeposition (Smulders et al. 2007). Miller and Raney (1993) note that, as with solubilisation, the important interaction is between the soil and the wash solution, and the fabric is less important.

Microcrystalline aggregates

A further mechanism of detergency involves surfactants penetrating into gaps in the layer of soil causing dislodgement of microcrystalline aggregates allowing the soil to break away from the fabric surface (Fort, Billica and Grindstaff, 1966 and Scott, 1963).

Liquid crystalline phase

If sufficient time is allowed, surfactants will penetrate any remaining oil and form a liquid crystalline phase (Dillan, Goddard and McKenzie, 1980). This will then be removed slowly by dispersion into the bulk solution, exposing a new interface for further removal. This mechanism is not generally

thought to be important in detergency as it has been found to take a minimum of a few hours to clean test surfaces.

If this mechanism is combined with solubilisation, the liquid crystalline phase can then be incorporated into micelles, which is a much more rapid process and this mechanism become significant (Miller and Raney, 1993).

Mass transfer

In the context of fabric washing, mass transfer is the process by which loosened soils are transported away from the fabric surface (Ganguli and Eendenburg, 1980). The loosened soil is first transported through the three-dimensional fabric structure of the fabric before diffusing into the wash solution. The mass transfer depends on the hydrodynamics of the rinsing process, whether by hand or in a washing machine. In the interyarn pores mass transfer occurs via convection. There will be little or no flow through the intrayarn pores, which will contain stagnant liquid, therefore mass transfer in these regions occurs by diffusion. During fabric washing the soil in the smaller pores will diffuse slowly into the convection region, where removal is much quicker.

2.6.3. Particulate soils

Removal of particulates depends on the location of the soil, contact area between the fabric and soil, and its adhesion to the fibres, rather than on the hydrophilicity of the fabric surface. The adhesion is generally due to Van der Waals forces. To remove the soil, the adhesive bond must be broken followed by wetting of the soil and fabric surfaces (Kissa, 1981a). Kissa (1981) noted that mechanical force is often required to break the adhesive bond; wetting of the fibre is not sufficient to do this. If the soil is not removed it is likely that there is either a strong adhesive force, or the location of the soil is not easily accessible (Kissa, 1979). The rate of removal of particulate soils is difficult to characterise due to the heterogeneity of the particles in terms of size, shape and chemical composition (Kissa, 1978).

2.6.4. Degrees of cleanliness

It should be noted that there are a range of degrees of cleanliness. In terms of fabric, incomplete cleaning can lead to accumulation of unwanted materials over many wash cycles. If oily soils are allowed to accumulate they can lead to graying of fabrics, and will then absorb particulate soils more easily on the surface. There are five target levels of cleanliness: atomically clean is cleanliness at the nano scale or above; biologically clean (sterile) means there are no microorganism or biological debris; chemically clean indicates no foreign materials that will affect chemical reactions; hydraulically clean indicates the level of fouling does not affect the transport processes (at micron-scale or above); and physically clean is no physically or optically detectable materials (Chew, 2004).

The degree of cleanliness depends on the criteria chosen and the sensitivity of method of evaluation used. In this work the focus is on the fabric being physically clean.

2.7. The wash process

2.7.1. Commercial washing

History

The activity of washing fabrics occurred in many early civilisations, and the process remained very much the same until the introduction of mechanical clothes washers. The first invention to aid fabric washing was the scrub board in 1797, but the first drum washing machine was not patented until 1850 (Fisher, 1850). The first electrically powered washing machine was produced in 1908, and was the first move away from manual to mechanical washing (Lin and Iyer, 2006).

Hand washing

Hand washing is still very common in some parts of the world where machines are not widely accessible, and it is still frequently used even when a washing machine is available (Pakula and Stammering, 2010). As well as soaking in detergent solution, hand washing often involves beating

and scrubbing the fabric, followed by a rinsing stage. Hand washing requires significantly less resource consumption and water temperature is usually ambient. It does, however, require more time and effort by the consumer. Water used for fabric washing can also be recycled, for example to water plants.

Washing machines

Washing machines are becoming more popular, with emerging markets such as China seeing a dramatic increase in sales of clothes washers (Lin and Iyer, 2006). Washing machines and washing habits differ globally leading to variable water, detergent and cloth ratio, temperature, water hardness and dosage of detergent, as well as different detergent compositions (Olsen and Falholt, 1998). Table 2.1 compares the washing machines used in three regions of the world.

Table 2.1. Comparison of washing machines from United States, Western Europe and Japan (Olsen and Falholt, 1998).

	United States	Western Europe	Japan
Machine type	v-axis top loader (agitator)	h-axis front loader (drum)	v-axis top loader (pulsator)
Water heating	External water heater	Electric internal heating by washer	Predominantly cold fill
Washing time (min)	8-18	20-60	5-15
Amount of water (l)	60-157	8-15	30-60
Temperature (°C)	10-40	30-95	5-25
Water hardness	Low/medium	Medium/high	Very low
Detergent dosage (g/l)	1-2	5-10	0.5
Average load size (kg)	3	2.8	2.5
Washes per week	6-11	5	10

In Europe, the majority of households now use horizontal drum or front loading machines. In these machines only the bottom of the drum is filled with water, sufficient to wet but not fully immerse fabrics, often 5-15 L per wash (Smulders et al. 2007). This allows for the use of less detergent. However, they do contain integrated heating systems so consume larger amounts of energy (Pakula and Stamminger, 2010). Mechanical action is provided by movement of the cylinder including the paddles on the drum, which lift the fabric up and allow it to fall due to gravity (Van Den Brekel, 1987).

Vertical axis or top loader machines are popular in North America and Asia, each with a different design. Fabrics are placed in a vertically mounted basket within a tub, and an agitator or impeller sits in the centre of the basket. The tub is filled with water, which can be up to 68 L in a single wash cycle (Bansal, Vineyard and Abdelaziz, 2011). These machines often use less energy, as water is supplied by an external heater, and the washing machine is only required to maintain the temperature (Golden et al., 2010). The movement of the agitator causes the water to move in a circular manner to increase flow through the fabric for cleaning, but its action can also cause additional wear and tear on fabrics.

Currently the washing machine sector is seeing some innovative improvements including the use of ultrasound or injection of bubbles during the wash cycle. The market is progressing further with the addition of microchip processors to adapt the wash cycle to the weight of the wash load and level of soiling.

2.7.2. Laboratory washing

A measure of detergency is of great importance due to the ongoing research to improve detergent formulations (Spangler, Cross and Schaafsma, 1965). When testing in the lab it is important to have a standardised soiling procedure and reliable, consistent visual or instrumental evaluation of soil level (Neiditch, Mills and Gladstone, 1980). Harris and Brown (1950) noted that it is also important that the strength of mechanical action and it's mode of application, time, and the ratio of fabric to soil

level and wash solution volume are controlled as all of these can affect the amount of soil removal. Previous testing has used a Terg-O-Tometer or Launder-O-Meter. Consumer tests also give a good indication of how well a product performs at home with the consumer (Smulders et al. 2007).

The Terg-O-Tometer, widely used in detergency studies, has been designed to replicate the action of an American agitator type washing machine, but on a much smaller scale (Gilman, 1989). The unit often consists of between 4 and 8 washing pots mounted in a water bath to allow temperature control. The benefits of a Terg-O-Tometer are that it provides accurate rapid results at low cost and don't require skilled operators (Linfield, Jungermann and Sherrill, 1962).

Han et al. (2015) investigated cleaning using the Terg-O-Tometer to provide mechanical action and found that cleaning performance was improved by increased detergent concentration and increased speed of agitation. A positive synergistic effect was also found when both were used simultaneously.

The standard laboratory washing machine of the American Association of Textile Chemists and Colourists is the Launder-O-Meter. The Launder-O-Meter consists of a rotatable container containing steel or rubber balls (Harris, 1952). The mechanical force can be altered by changing the number and size of steel balls in the vessel, and by changing the speed of rotation (Bacon and Smith, 1948).

Both the Terg-O-Tometer and Launder-O-Meter are useful for small-scale studies where replication of a washing machine is required for high throughput comparison of test formulations. However, they do not allow individual study of mechanical action, chemical action and temperature, therefore mechanistic understanding of the cleaning process is not possible.

2.8. Analysis techniques

A number of techniques have been used to characterise fabrics and soils in current literature. Some techniques, such as FDG, have been used on other surfaces including membranes, but their use on

fabrics is novel to this work. When used individually, the techniques outlined give interesting information about fabric cleaning, but a complete picture is only found when the techniques are used in combination.

2.8.1. Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) is a useful technique for studying deposits on a surface. The technique involves passing radiation, typically in the range 4000 to 600 cm^{-1} , through a sample. Some radiation will be absorbed by the sample while some will be transmitted. The resulting spectrum gives absorption peaks, which correspond to the frequency of the vibrations of the bonds in the molecule (ThermoFisher Scientific, 2016). Bonds that are more ionic in nature show characteristic peaks with strong FTIR signals, which can be easily identified. This gives rise to a particular fingerprint allowing positive identification of a molecule. Each frequency can be measured simultaneously, rather than individually, and the raw data is converted to a spectrum by Fourier Transform. The benefits of IR include that it is nondestructive, does not require external calibration and is a relatively quick and low cost technique, however spectra often only provide qualitative results (Klages and Grishin, 2008). FTIR was used to characterise the surface of the unsoiled sample as well as investigate cleaning by measurement of soiled and cleaned samples.

2.8.2. Contact angles

Theory

The wettability or hydrophobicity of surfaces is important to aid understanding of soiling and cleaning. Generally, more hydrophobic surfaces tend to soil more easily as they have a greater affinity for oily materials. The contact angle can be used as a measure of hydrophobicity. A drop of liquid on a solid surface can remain as a drop or spread out infinitely over the surface. Whether the liquid stays as a drop or spreads is dependent on the balance between the surface energies of the

solid-liquid (γ_{SL}), solid-air (γ_{SA}) and the liquid-air (γ_{LA}) interfaces (Cassie, 1948). The condition for spreading is shown in Equation 2.3.

$$\gamma_{SA} - \gamma_{SL} > \gamma_{LA} \quad \text{Equation 2.3}$$

If this is not the case and the liquid remains as a drop on the surface it will form an angle, θ , at the intersection of the liquid-solid interface and liquid-air interface, as in Young's Equation (Equation 2.4).

$$\cos\theta = \frac{\gamma_{SA} - \gamma_{SL}}{\gamma_{LA}} \quad \text{Equation 2.4}$$

When a droplet spreads out, a small contact angle is observed, which shows high wettability and shows the surface is hydrophilic. If the liquid beads on the surface and has a large contact angle this shows low wettability, and a hydrophobic surface (Yuan and Lee, 2013). This can be seen in Figure 2.8.

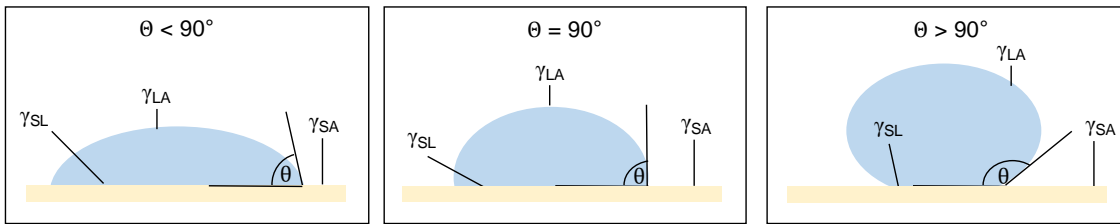


Figure 2.8. Contact angles, θ , showing the three interfaces of interest; the surface energies are given by γ_{SL} for the solid liquid interface, γ_{SL} for the solid air interface and γ_{SA} for the solid air interface. Adapted from Yuan and Lee (2013).

As drops may not be symmetrical the contact angle is measured on both sides and an average taken.

For fabrics, the contact angle can be affected by many factors including the material, the roughness of the surface and any coatings added by the manufacturer, as well as the purity of the water used.

Measurements are taken as comparative rather than absolute values.

Experimental techniques

Traditionally contact angles are found using the sessile drop method. A drop of pure water is placed on the solid surface using a syringe and the contact angle is calculated from a computer image. This process is repeated 10 times, calculating the angle on both sides of the drop. This method requires the surface to be dry prior to testing.

Alternatively, the captive bubble technique can be used. This involves trapping an air bubble at the solid surface, which is inverted and submerged in water. The benefit of this method is that it is possible to get an idea of the properties of the fabric when it's wet; when dry, surface properties will be different (Zhang and Hallström, 1990). Also, there is less risk for contamination and no issue of evaporation of the water droplet. However, Drelich and Miller (1993) found that the results are generally more scattered than those obtained using the sessile drop method.

The advantages of using contact angles by sessile drop or captive bubble methods is that it is a simple measurement to take, and only small amounts of fabric are required. However, Yuan and Lee (2013) found that assignment of the base line affects the tangent taken for the contact angle, which may be problematic.

The contact angle is known to be affected by the roughness or heterogeneity of the surface. Surface roughness causes deformations in the bubble at the three-phase contact line, which affect the free energy of the liquid drop or gas bubble (Drelich, Miller and Good, 1996). This leads to difficulties as what is measured is the apparent contact angle, the angle between the direction of the tangent and the seemingly smooth surface, which is different to the actual contact angle, the angle between the tangent and the direction of the rough surface at that point. If the surface is smooth, the apparent and actual contact angles will be equal (Marmur, 2000).

Alternative techniques

To avoid this issue it is possible to find contact angles of individual fibres, however we are interested in the properties of the surface as a whole, not of individual fibres. Yuan and Lee (2013) found that the apparent contact angle can be misleading if the drop diameter is much larger than that of the fibre. Zhu et al. (2005) reported that the contact angle of fibres is less than that of the fabric.

It may be possible to study hydrophilicity by examining sinking time of fabric, vertical sorption over a water bath or horizontal spreading of water (Kissa, 1981a). Sinking time is measured by placing the fabric on the surface of a liquid and calculating the time taken for the fabric to sink. The time taken will depend on hydrophobicity of the fabric as sinking is dependent on the amount of liquid that diffuses into the fabric, replacing air. Kissa (1981) noted that sinking time is not directly related to the wettability of the fabric as it is also affected by the geometry of the fabric and of the fibres. Hsieh (1995) used vertical sorption, where a strip is hung vertically above a large water bath and the amount of water diffused into the fabric determined. This can be measured by attaching the hanging fabric to a microbalance. The final method involves dropping a known amount of liquid on to the fabric surface and determining the area formed as the drop spreads as a function of time (Kissa, 1975).

2.8.3. Atomic Force Microscopy

Atomic Force Microscopy (AFM) can be used to characterise the surface structure and topography, and has been used extensively to investigate pore size distribution, porosity and surface roughness of membranes (Chan and Chen, 2004). Surface roughness is important for soiling, as Hoek, Bhattacharjee and Elimelech (2003) report that a rougher surface leads to greater soiling as soil can get trapped in the troughs.

For AFM measurements, a sharp probe or tip is attached onto a flexible microscopic cantilever and moves vertically. A laser beam is focused on the back of the cantilever, and deflected to a dual

element photodiode. The laser reflection is plotted against tip height, giving an accurate picture of the topography of the surface as the three dimensional map. Images of the surface are produced that show nanometer scale features, and resolution can reach atomic dimensions for flat surfaces (Bowen et al. 1998). In contact mode the tip touches the surface as the probe moves across it, so the externally applied spring force must be greater than the repulsive forces, whereas in non-contact mode the tip responds to forces between the tip and the surface without touching it. Finally, in tapping mode, the tip vibrates over the surface with a predetermined force. This is the standard mode of operation. Benefits of AFM include its ability to image non-conducting materials in air or liquid without extensive sample preparation, (Bowen et al., 1998) and resolution is higher than that found with electron microscopy (Bowen and Doneva, 2000).

Bowen et al. (1998) reported use of atomic force microscope with a colloid probe rather than a tip to quantify interactions between a particle and a membrane surface. The colloid probe consisted of a polystyrene or silica sphere attached to the end of the cantilever. The probe is moved close to the surface at a controlled rate, and then retracted again. This gives the force of adhesion of a single particle in the direction normal to the membrane surface, and both surface forces and molecular forces can be investigated. This technique is fast and measurements can be made in solution. It is thought that this technique will apply equally well to quantification of forces between soil particles and fabric surfaces. Llanos et al. (2010) concluded that these measurements could be qualitatively analysed to predict membrane fouling tendency.

2.8.4. Zeta Potential

The surface charge on a surface can aid prediction of its soiling tendency. Zeta potential, ζ , has been used to quantify the charge density of a membrane surface (Chan and Chen, 2004). Surfaces such as membranes become charged in aqueous solution by dissociation of functional groups, adsorption of ions from the solution, or adsorption of molecules including surfactants (Schaep and Vandecasteele, 2001). This in turn affects the distribution of ions in the vicinity of the surface to achieve overall

electroneutrality (Kim et al. 1996). The concentration of counter ions close to the surface decreases with increasing distance from the surface. This produces a variation in electric potential between the surface and the bulk solution (Jones, 2012), which forms an electric double layer; a charged surface and an excess of counter ions in solution near to the surface known as the Stern layer, as shown in Figure 2.9. Other counter ions exist in the diffuse layer, hence the name double layer.

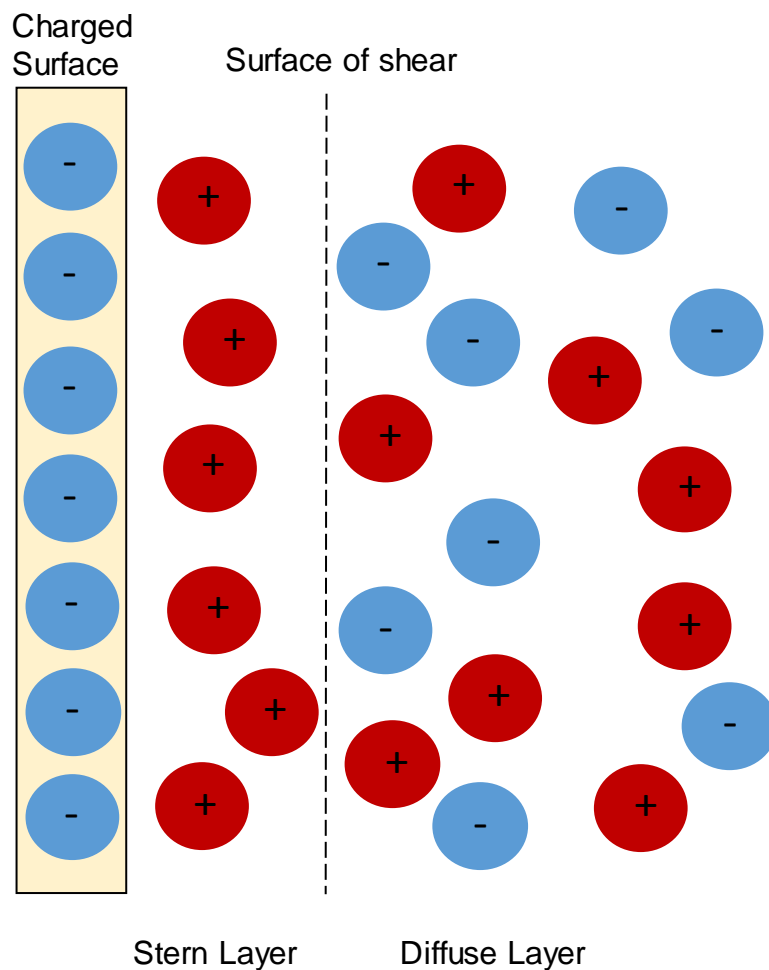


Figure 2.9. Diagram of electric double layer.

The electric double layer theory assumes ions close to the surface remain stationary, meanwhile the diffuse layer moves with the flow. The plane between this stationary layer and diffuse layer is known as the surface of shear. The potential difference between these two layers at the surface of shear is known as the zeta potential. The thickness of the Stern layer depends on the type and concentration of ions in solution.

Zeta potential cannot be directly measured, but can be calculated when the streaming potential, ΔE_s , is found. The streaming potential is the potential generated when ions in the diffuse area of the double layer move under an applied field, and ions adjacent to the surface remain stationary. The potential is generated in the opposite direction to the flow of ions. The Helmholtz-Smoluchowski Equation, Equation 2.5, is used to calculate zeta potential from the streaming potential.

$$\zeta = \frac{\Delta E_s \eta \kappa}{\Delta P \epsilon \epsilon_0} \quad \text{Equation 2.5}$$

where η is the solution viscosity; κ is the conductivity of the solution; ΔP is the pressure difference across the channel, ϵ is the permittivity of the solution; and ϵ_0 is the permittivity of vacuum. Mänttari, Pihlajamäki and Nyström (2006) found that the Helmholtz-Smoluchowski Equation was accurate for smooth, homogeneous and non-conducting surfaces, but fabrics are not smooth surfaces. Attempts have been made to apply corrections to the Helmholtz-Smoluchowski Equation, however if all measurements are taken under the same conditions, this gives zeta potential values that are comparative rather than absolute values, which is sufficient for understanding surface charges (Nyström, Pihlajamäki, and Ehsani, 1994). This is due to the fact that the pores are not cylindrical, and not large enough to prevent overlapping of electric double layers, which prevents free passage of electrolyte. Streaming potential measurements can be taken with electrolyte flowing through the pores or across the surface (Deshmukh and Childress, 2001).

Zeta potential measurements are found over a pH range, often 3 to 8. This aids understanding of the acid-base properties of the surface. Huisman et al. (1998) reported that many membranes have negative zeta potentials at high pH and positive zeta potentials at low pH. The point where the zeta potential equals zero is known as the isoelectric point (Szymczyk et al., 1998). One limitation of the technique is that the system is restricted to a moderate pH range, therefore it is not possible to use aggressive chemicals.

2.8.5. Resistance measurements

Another measure of cleanliness could be resistance to flow. It is thought that a more soiled fabric will have a higher resistance, as the soil will sit within the pores restricting the flow of water. The flow through a fabric can be understood using Darcy's Law, often applied to membranes, which states that the flux is proportional to the driving force, and inversely proportional to the resistance and viscosity, as shown in Equation 2.6.

$$Flux = \frac{Driving\ Force}{Resistance \times Viscosity} \quad \text{Equation 2.6}$$

If the solvent is freely transferable through the membrane, flux, J_V , can be described using Equation 2.7.

$$J_V = \frac{\Delta P - \Delta \pi}{\mu R_M} \quad \text{Equation 2.7}$$

where ΔP is trans membrane pressure, $\Delta \pi$ is osmotic pressure, μ is viscosity of the solution and R_M is the hydraulic resistance of the membrane, or fabric in this case. Osmotic pressure, π , can be considered negligible due to the pore size. Since flux, J , is equal to volumetric flow rate, Q , over surface area, A , resistance change is given by Equation 2.8.

$$R_M = \frac{A \Delta P}{\mu Q} \quad \text{Equation 2.8}$$

where A is the area through which flow is permitted, ΔP is the pressure drop across the cloth ($N.m^{-2}$), μ is the fluid viscosity and Q is the volumetric flow rate ($m^3.s^{-1}$). This measurement is independent of sample thickness, which may change due to swelling during an experiment. It is suspected that the swelling may decrease pore size, but that this will not be significant compared to pore blockage by the soil.

2.8.6. Reflectance measurements

Reflectance can be used as a measure of cleaning efficiency. This is measured with a spectrophotometer and gives a change in reflectance of the fabric surface. Harris, Sullivan and Weeks (1954) noted that the limitation with this measurement is that it assumes the amount of light absorbed is proportional to the concentration of soil on the fabric, which has been shown to be false, and Lambert and Sanders (1950) discussed the nonlinear relationship between reflectance and quantity of soil of the fabric surface.

For this reason, Strain Removal Index (SRI) is often used. This takes into account the reflectance of the unsoiled fabric, as well as the soiled and washed fabric, as shown in Equation 2.9.

$$SRI = \frac{A-B}{C-B} \times 100 \quad \text{Equation 2.9}$$

where A is the average reflectance of soiled cloth after washing, B is the average reflectance of soiled cloth before washing and C is the average reflectance of white cloth before soiling (Gilman, 1989).

2.8.7. L*a*b* measurements

An alternative measure of cleanliness using colour is the L*a*b* scale. L* gives an indication of lightness where a low number (0 to 50) indicates darker colour and a high number (51-100) indicates a lighter colour. For the a* axis, red gives a positive number and green gives a negative number. Finally, for the b* axis, yellow gives a positive number and blue gives a negative number (HunterLab, 2001). This is shown in Figure 2.10.

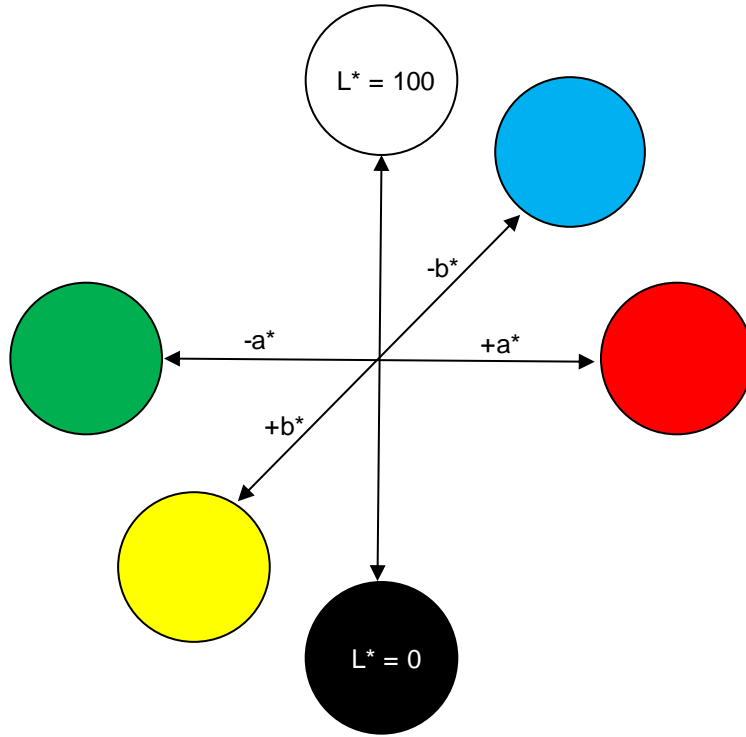


Figure 2.10. L^* a^* b^* colour space. L^* gives a higher number for lighter colours. A more positive a^* means a more red color, and a more negative a^* means a more green colour. A more positive b^* means a more yellow colour, and a more negative b^* means a more blue colour. (Adapted from HunterLab, 2001)

Numbers can be given as absolute L^* , a^* and b^* values, or as delta values to show the difference of the sample from a standard or other reference. In this report, Δa^* and ΔL^* values of the washed fabric are compared to the soiled unwashed fabric. Δa^* gives the change in redness, a more positive a^* values indicates a more red fabric so a more negative Δa^* indicates more sebum removal. L^* gives a higher value for lighter coloured fabrics, so a more positive ΔL^* indicates more sebum removal.

ΔE is also used as a measure for soil removal when a single number is required, and is based on overall colour difference (Neiditch, Mills and Gladstone, 1980). Equation 2.10 shows calculation of ΔE . The average person would notice a colour difference with a difference greater than four, whereas a trained observer would be able to notice a colour difference when the ΔE value is greater than two (Cruse, 2016).

$$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2} \quad \text{Equation 2.10}$$

2.8.8. Gravimetric method

Gravimetric measurements are also possible, so long as the fabric surface has not been contaminated by unwanted matter and there has not been significant loss of fibres during washing. It is important to measure the fibre at the same level of moisture before and after cleaning, particularly with cotton due to its hygroscopic nature. To do this the fabric must be kept in humidity-controlled conditions or dried prior to measurement.

2.8.9. Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) analyses the materials heat capacity (C_p) with respect to temperature, giving information about transitions including melting, phase changes and glass transitions (PerkinElmer, 2013). This aids understanding of amorphous and crystalline behavior, and polymorph and eutectic transitions. Measurements are compared to a reference sample, and the amount of heat required to increase the temperature of both samples is measured as a function of temperature. At the point the sample undergoes a physical change more or less heat will be required compared to the reference to maintain both samples at the same temperature. This provides information as to whether the process is exothermic or endothermic. DSC gives both the temperature at which melting begins, but also the peak temperature, corresponding to the temperature at which complete melting is achieved. Advantages of DSC include ease and speed of measurements.

2.8.10. Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) is a common technique used to image surfaces, which has been extensively used to study membrane fouling and cleaning (Hayward, 2015). Cleaned surfaces, such as fabrics, can be compared to virgin and soiled surfaces to visually assess cleaning. A focused beam of electrons, applied under vacuum, excites atoms on the surface and secondary electrons are produced. These are detected and used to produce a detailed image of the surface.

2.8.11. Direct observation through the fabric surface

Direct observation through a membrane as a technique to study fouling layers was outlined by Jones (2012) and Mendret et al. (2007). This technique involves observing deposition of foulant during cross flow experiments. The experimental set up including an optical microscope capable of using both transmitted and reflected light sources attached to a video camera. This technique requires a relatively transparent membrane, so cannot be used for fabrics. Additionally, observation is limited to the first layer of the deposit, therefore in cleaning experiments it would only be observed when the surface had been completely cleaned, and information about cleaning up until this point would not be possible.

2.8.12. Laser triangulometry

Laser triangulometry, used by Schluep and Widmer (1996), can be used to track the growth of a fouling layer, and to measure the thickness of this layer. This technique involves shining laser light through a window in a cross flow rig, and the reflection of this laser beam is captured by a camera. The deflection of this laser gives information about the buildup or removal of a fouling layer. Chen, Li and Fane (2004) noted that this technique showed limited resolution, and doesn't aid understanding of particle-membrane interactions.

2.8.13. Fluorescence and radioisotope techniques

Chen, Li and Fane (2004) discussed the use of fluorescence or radioisotope labeled proteins, to investigate fouling and cleaning at resolutions beyond those achieved with an optical microscope. A limitation of these techniques is that they require the labeled species to behave in the same way as the unlabeled substrate. The techniques also require calibration of the signals.

2.8.14. Fluid Dynamic Gauging

Fluid dynamic gauging (FDG) was developed by Tuladhar et al. (2000), as a technique to determine the thickness of deposits and give an estimate of adhesive and cohesive forces of these deposits. It shares similarities with pneumatic gauging, where the pressure drop of a gas expelled through a nozzle is used to study the surface perpendicular (Evans and Morgan, 1964). FDG, on the other hand, involves suction of a fluid in which a soiled surface has been submerged through a nozzle. Initially used on hard surfaces (Chew, 2004), recent work has extended its use to membranes (Jones, 2012 and Lewis, 2015). FDG can be used in both static and flow environments. The main features of FDG are that it allows measurements in-situ and in real time, as well as being robust, simple and effective.

The general principle of FDG is rooted in fluid mechanics, based around the fact that pressure drops when flow is directed through a constriction and subsequent divergence, such as through a nozzle, as shown in Figure 2.11. The FDG set up consists of a nozzle, diameter d_i , fixed on to a tube, diameter d , placed normal to a surface. Close to the surface, ca. $h/d_i < 0.25$, the fluid flow into the nozzle, m_{gauge} , and pressure drop across the nozzle, ΔP_{gauge} , depend on its distance from the surface. This is known as the incremental zone, and is the region in which FDG thickness measurements can be made. Outwith this region, flow is limited by the nozzle diameter, d_i , therefore is no longer useful for thickness measurements.

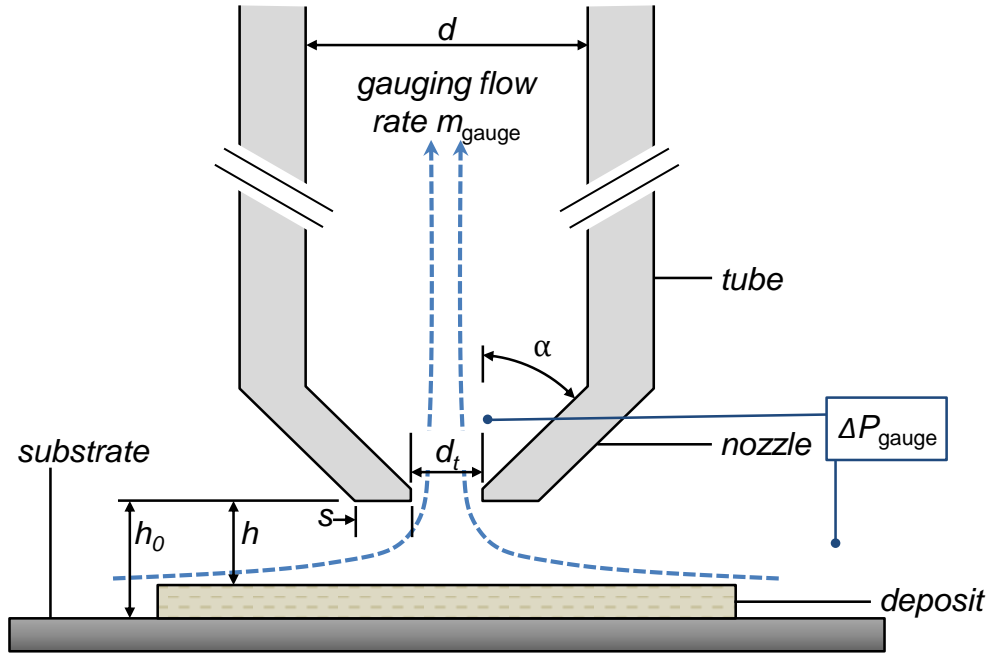


Figure 2.11. Schematic of FDG consisting of a nozzle of diameter d with tube diameter of d_t , internal angle α and wall thickness s . The nozzle is positioned at a known distance, h_0 , from a surface. Mass flow and pressure measurements can be used to determine the distance from the nozzle to the deposit, h , and hence the thickness of the deposit can be calculated. Adapted from reference (Chew, Paterson and Wilson, 2007).

FDG can be used in two modes; mass flow mode and pressure mode. Mass flow mode, originally developed by Tuladhar et al. (2000), used hydrostatic pressure to generate a measureable flow rate, m_{gauge} , which was then used to calculate h . Using this method, control of the flow rate is not possible, and practical difficulties such as accurate measurement of the expelled flow led to the development of pressure mode (Lewis, 2015). In this work pressure mode FDG was used, in which mass flow rate through the nozzle is controlled, and the pressure drop across the nozzle, ΔP_{gauge} , is measured (Lister et al., 2011). This allows experiments at higher flow rates and better control over the rate of removal.

Initially, a calibration plot is produced for the clean surface, allowing conversion of the pressure drop into the dimensionless distance from the deposit surface, h/d_t . The deposit thickness, δ , is then calculated by subtracting the h value from the offset, h_0 . FDG can also be used for strength measurements. The shear stress imposed on the surface, τ_w , can be approximated using Equation 2.11 (Chew et al., 2004).

ΔP_{gauge} is measured and the calibration plot used to find h , as above, which is then used to calculate τ_w .

$$\tau_w = \frac{3\mu m_{gauge}}{\rho\pi h^2 r} \quad \text{Equation 2.11}$$

where μ is the dynamic viscosity, ρ is the density of the fluid and r is the radius of the nozzle.

Fluid Dynamic Gauging has been used for a wide range of applications. Gordon et al. (2010) studied thickness and strength (adhesion and cohesion) of gelatin layers with commercial dishwasher formulations. Jones et al. (2012) reported the use of FDG to track the thickness of cake formation on a microfiltration membrane fouled with sugar beet molasses, and subsequent cleaning of the membrane. Simultaneously, flux measurements were made to allow understanding of the makeup of the cake layer. Peck et al. (2015) used FDG to study the adhesion of *Escherichia coli* biofilms grown on polyethylene, stainless steel and glass plates.

Peralta, Chew and Wilson (2011) examined the effect of external nozzle geometry to maximise either normal force or shear stress using computational fluid dynamics. All nozzles had the same internal geometry. Figure 2.12 shows dimensionless pressure profiles (normal force) for a variety of nozzle geometries. Nozzle N1 maximises normal force when $\theta = -15$. The profiles of dimensionless shear stress are shown in Figure 2.13. Nozzle N1 maximises shear stress when $\theta = -5$.

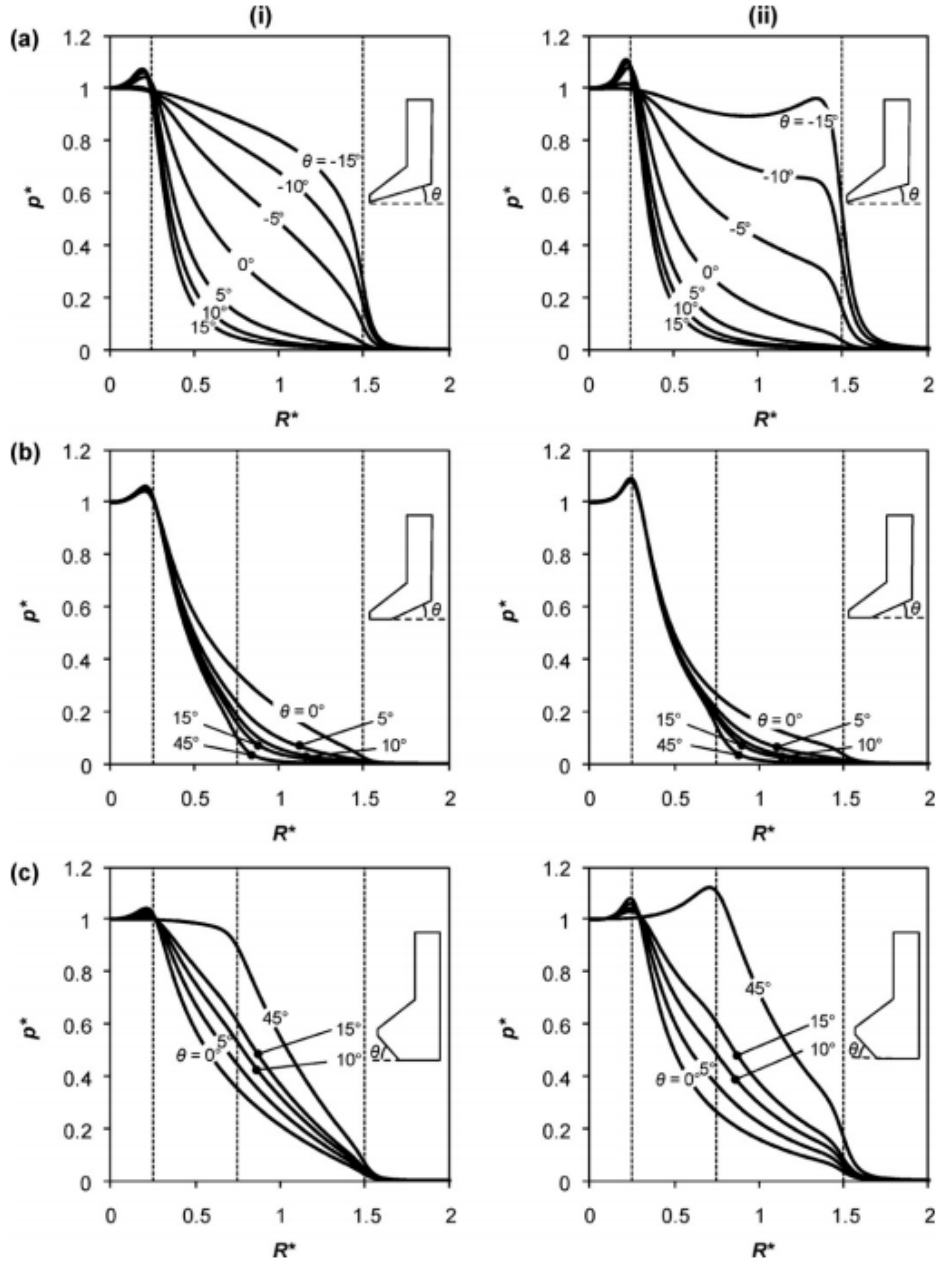


Figure 2.12. Dimensionless pressure profiles for different values of θ at $h/d_t = 0.2$. Nozzles: (a) N1, (b) N2, (c) N3: (i) $Re = 50$, (ii) $Re = 500$. Vertical dashed lines indicate the location of the outer and inner rim of the nozzle, or a position of a transition on the nozzle surface (Peralta, Chew and Wilson (2011)).

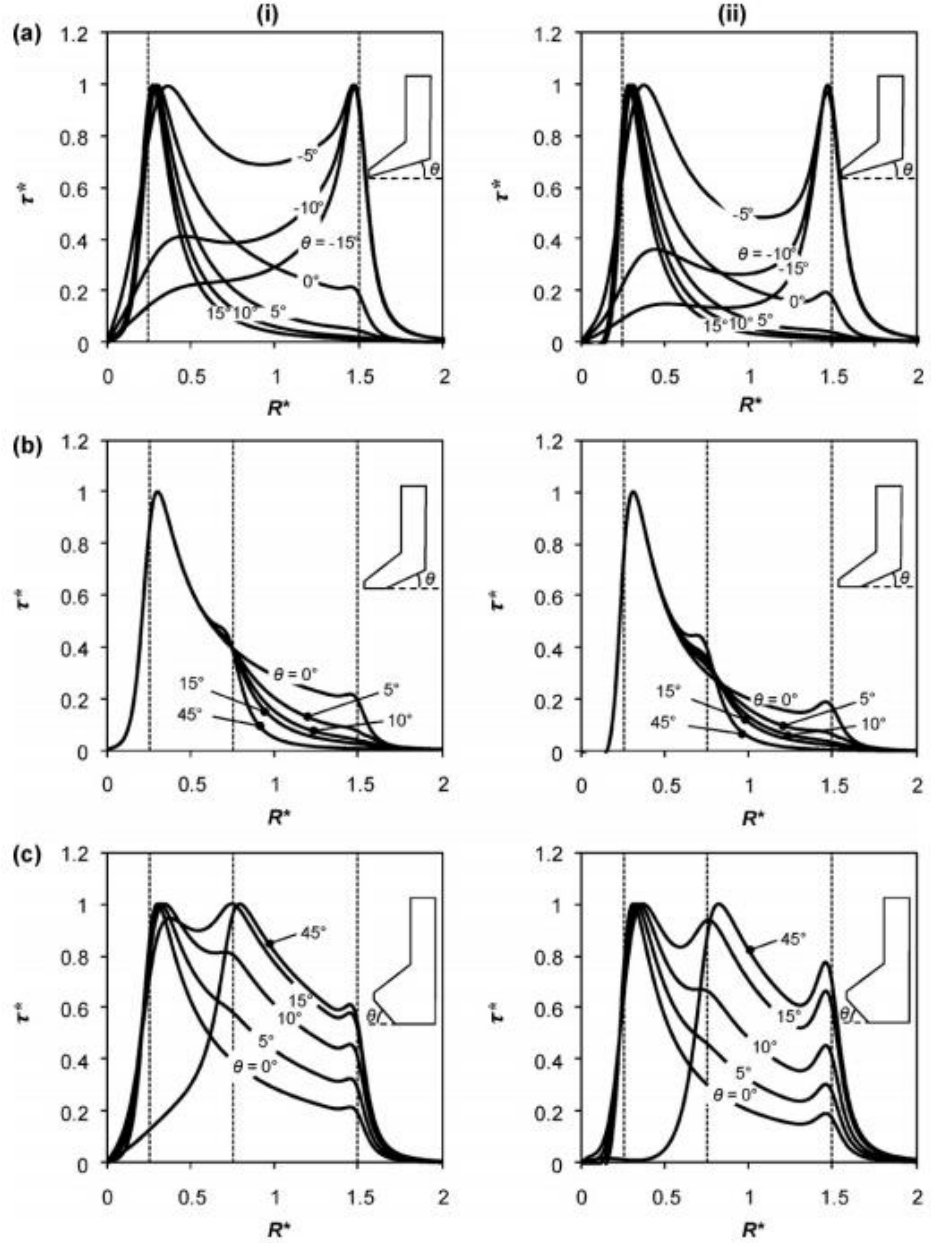


Figure 2.13. Dimensionless shear stress as a function of dimensionless radial position for different values of θ at $h/d_t = 0.2$. Nozzles: (a) N1, (b) N2, (c) N3: (i) $Re = 50$, (ii) $Re = 500$. Vertical dashed lines indicate the location of the outer and inner rim of the nozzle, or a position of a transition on the nozzle surface (Peralta, Chew and Wilson (2011)).

Figure 2.14 shows the dimensions of the nozzles that have been constructed for this work, to maximise normal force ($\beta = 15^\circ$) and shear stress ($\beta = 5^\circ$).

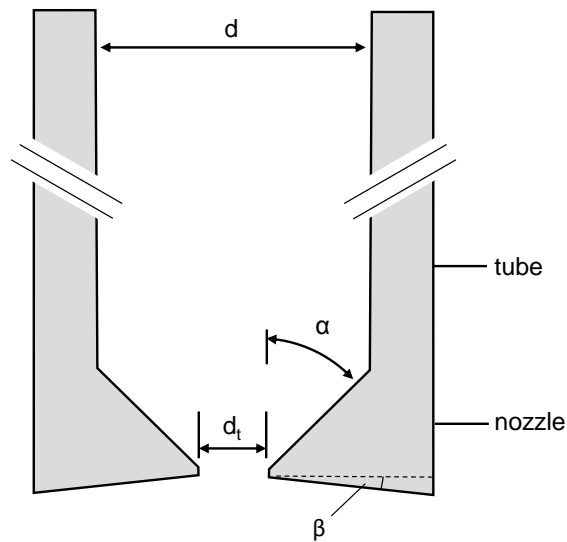


Figure 2.12. FDG nozzle with dimensions $d = 25$ mm, $d_t = 5$ mm, $\alpha = 30^\circ$, $\beta = 5^\circ$ or $\beta = 15^\circ$.

2.9. Summary

Clothes washing has been identified as an environmental issue due to the use of water, energy and chemicals in the process, and the frequency of clothes washing operations. Temperature has been identified as a major contributor to the amount of energy used, and reductions in temperature have been found to greatly decrease the energy used in the wash process. Although some work has been done to investigate the individual actions involved in fabric cleaning, deeper understanding of the mechanisms involved is still lacking. Bespoke equipment has been produced in Bath, but optimisation of equipment and methods were required prior to in depth testing and analysis.

Chapter 3: Materials and Methods

In this chapter the materials and methods used in this thesis are discussed. This includes choice of soil, fabric, wash solution and water, as well as a description of the bespoke equipment used throughout the work. Finally, methods used for analysis of virgin, soiled and cleaned fabrics are presented.

3.1 Materials

3.1.1. Fabrics

Industry standard fabrics were used. Initially, a plain weave woven polycotton (*Centre for Testmaterials BV*, W-20A) containing 65 % polyester and 35 % cotton by weight was used. This fabric was used for all proof of concept work.

It was then decided that fabrics used would be changed to match those used in testing by Unilever, Port Sunlight. Single fibre fabrics were chosen to isolate the effects of cleaning on different materials. The two fabrics selected were Knitted Polyester (100% Polyester, Yarn Count 78's/36's) and Woven Cotton (100% Cotton, 60 x 60 threads per square inch with 20 x 20 size yarns). Figure 3.1 shows simplified schematic diagrams of the two fabric structures, and identifies the fibres, yarns and pores. The main body of results in this thesis used these fabrics.

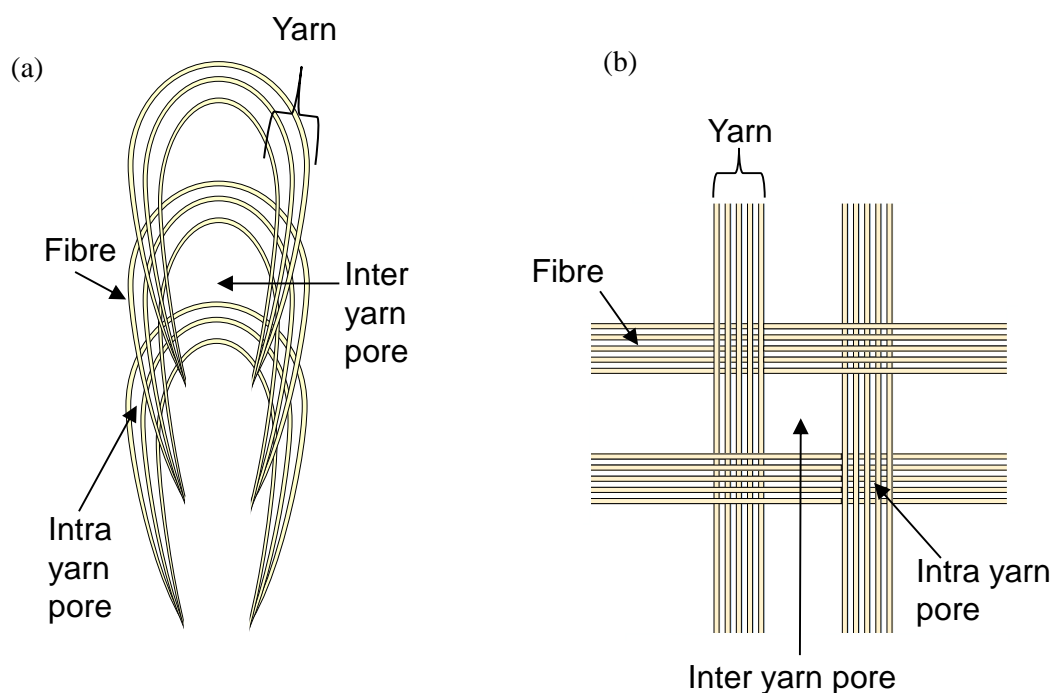
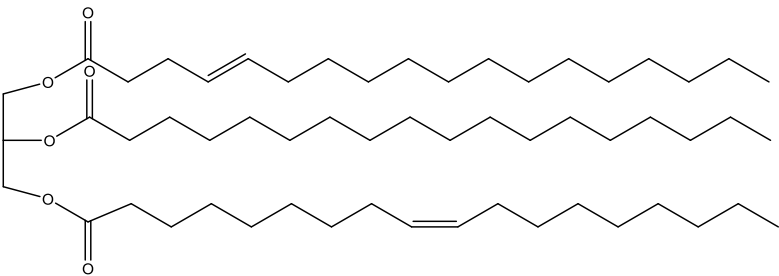
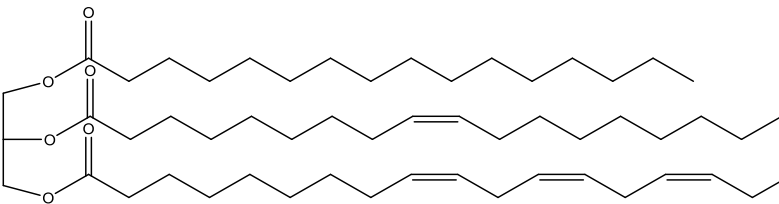
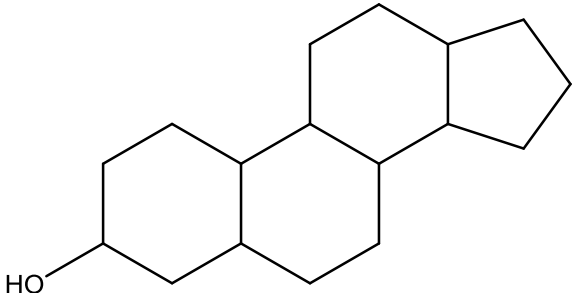


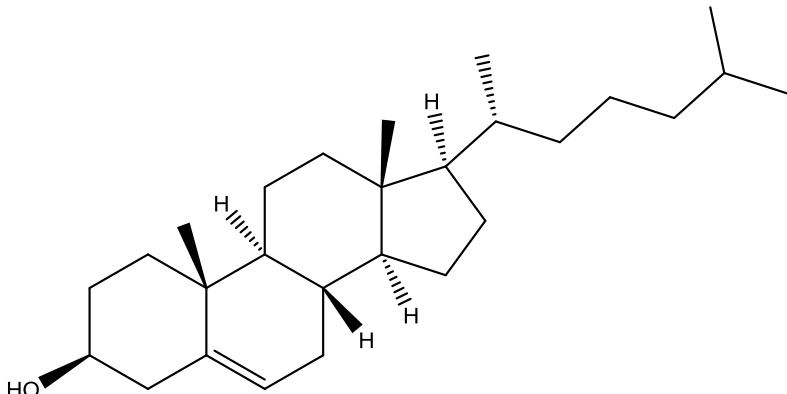
Figure 3.1. Schematic diagram showing structure of (a) polyester and (b) cotton fabric.

3.1.2. Soils

Artificial sebum was used in all testing. It was chosen as it is both a common and problematic stain, particularly in Developing and Emerging Countries (Wolff and Showell, 1997). It is not possible to use real sebum as it is highly variable and extraction of isolated sample of pure sebum from human skin would be very difficult. The composition of the artificial sebum used is outlined in Table 3.1.

Table 3.1. Constituents of artificial sebum (Lu et al., 2009)

Constituent	Amount (%)	Description
Carboxylic acids	18	Organic molecules with the general formula RCOOH. Also known as volatile fatty acids or free fatty acids.
Beef tallow	32.8	<p>Consists mainly of triglycerides, whose major constituents are derived from stearic and oleic acids. In this context, tallow is animal fat that conforms to certain technical criteria, including its melting point.</p> 
Triglycerides	3.6	<p>Esters derived from glycerol with three carboxylic acids.</p> 
Lanolin	18.3	<p>A mixture of esters including sterol esters found in sheep's wool.</p> 

Cholesterol	3.7	<p>An organic molecule that is both a sterol and a lipid, and is biosynthesised by animal cells.</p> 
Hydrocarbon mixture	12	Organic compounds consisting entirely of carbon and hydrogen.
Cutina	11.6	A polyester polymer of indeterminate size, interlinked via ester bonds. Monomer units are often C16 or C18.

3.1.2.1. Application method 1

Artificial Sebum produced according to BEY composition (*Materials Research Products*, 00612) was prepared by addition of Oil Red O dye (*Sigma Aldrich*, O0625) at a concentration of 0.5 mg.L^{-1} . Sebum was melted on a hotplate (*Cole Palmer*, StableTemp, adapted to accommodate size of fabric) at 300°C until all solid matter had melted and for a further 5 minutes before addition of the dye. Sebum was then stored in a freezer (*Miele*, F12020S-2) at -18°C . Aliquots of the dyed sebum were then heated and added to a 60 mL syringe and stored in a refrigerator (*Miele*, F12020S-2) at 3 to 5°C for a maximum of one month.

Fabrics were preconditioned to remove any sizing agents by washing once with ECE powder (90 g) provided by Unilever on a 40°C short cotton wash for 90 minutes in a domestic washing machine (*Miele*, Novotronic W1614) with cotton ballast. This wash cycle was then repeated with no detergent. Fabrics were dried in a domestic tumble dryer (*Miele*, Novotronic T7644 C) for 30 minutes then transferred to a washing line for the final stages of drying. This was consistent with protocols used by Unilever. Fabrics were then cut to a size of $355 \times 125 \text{ mm}$.

Fabrics were weighed on an analytical balance (*Adam Equipment*, PW254) and the mass recorded by a data logging computer. The fabric was transferred to a pre-heated adapted hot plate which allowed the whole sample to lie flat. The fabric was heated at 115 °C for 15 minutes before reweighing. Reweighing produced a curve as the sample absorbed moisture from the air after removal from the hotplate. It was then placed back on the hot plate for 5 minutes and reweighed twice to obtain three 'dry' mass curves. The fabric was placed back on the hot plate and a thin line of soil of 744 ± 20 mg was added from the syringe using a mastic gun down the centre of the long length of the fabric and allowed to soak in before a final mass measurement was taken. A MATLAB script was used to fit curves to the three dry mass curves to determine the average dry mass of the cloth and to the soiled mass measurement to calculate the soil mass.

The fabric was then imaged using a camera (*Nikon*, Coolpix L310) in three different orientations. The total cloth area and fouled area were calculated by a MATLAB script (Muir, 2011). Using this and the soil mass, the mass of soil per unit area could be calculated. The average mass per unit area of soil was found to be 6.69 ± 0.40 mg.cm⁻². Fabrics were also imaged using a Spectrophotometer (*Datacolour*, Spectraflash 600 PLUS). Fabrics were then stored in the refrigerator at 3 to 5 °C and consumed within one month of preparation, as had been done in previous tests (Muir et al., 2013).

Figure 3.2 shows the (a) topside and (b) underside of the fabric when this application method is used. All proof of concept work used this method of application.

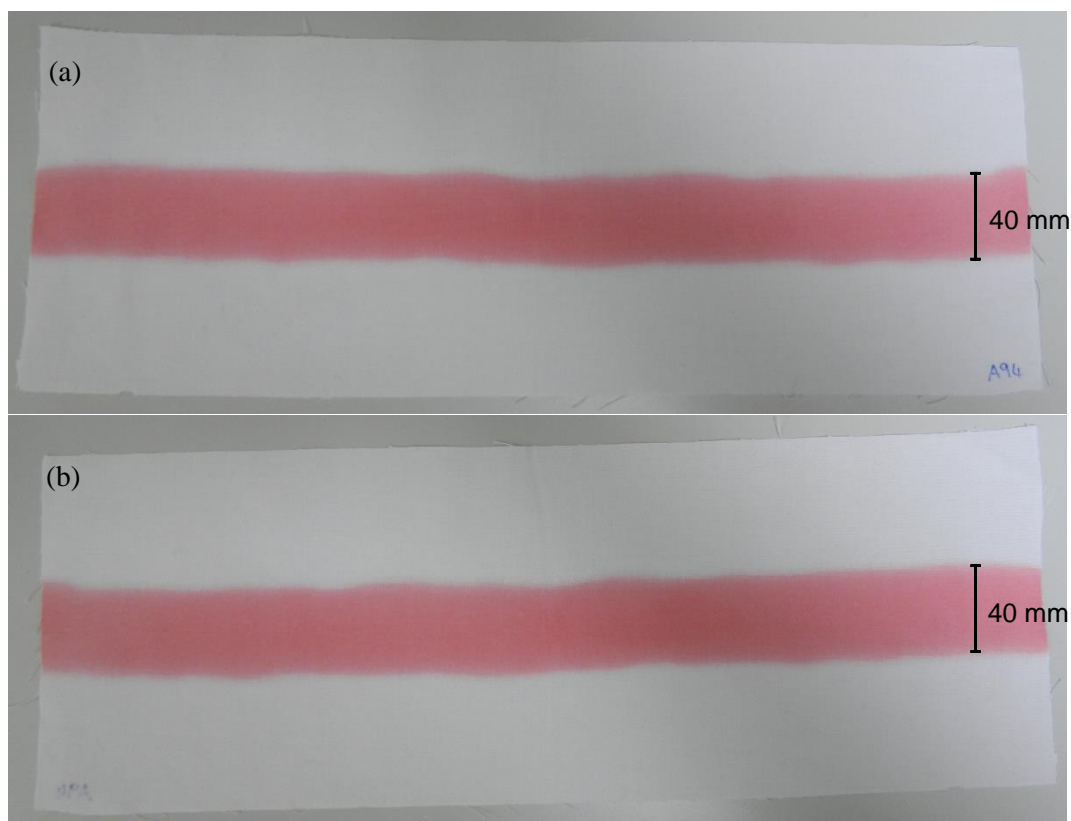


Figure 3.2. Images of the (a) topside and (b) underside of polycotton soiled with sebum using application method 1.

3.1.2.2. Application method 2

Synthetic sebum (wfk, 00612) was heated to 40 °C prior to addition of Oil Red O dye (*Sigma-Aldrich*, O0625) at a concentration of 1 g.kg⁻¹.

Fabrics were prepared by *Equest*. The fabric was taped to a solid surface and the sebum was applied with a sponge applying the same weight along the central 40 mm length of the fabric. Once stained the fabric was stored in a dark room at room temperature to dry before being vacuum packed and transferred to the fridge.

Figures 3.3 and 3.4 show the (a) topside and (b) underside of polyester and cotton respectively, soiled using application method 2. The front and back of polyester look almost identical, suggesting the sebum has permeated the fabric, whereas there are distinct differences between the topside and underside of cotton indicating most of the sebum remains on the top surface.



Figure 3.3. Images showing the (a) topside and (b) underside of polyester soiled with sebum using application method 2.



Figure 3.4. Images showing the (a) topside and (b) underside of cotton soiled with sebum using application method 2.

3.1.3. Surfactants

Solutions were formulated based on the CMC of LAS, with one solution 2 x CMC and the other 0.1 x CMC of LAS. A standard dose of detergent is 35 ml in 5 L. For 500 L, a solution of 3.5 L was made containing the amounts of LAS and other components listed in Table 3.2. The amount of LAS required was first calculated. The CMC of LAS is 0.0016 mol.L⁻¹, and the Mr is 348. Other components were calculated based on weight percent and added to give a total of 3.5 L of detergent solution.

Table 3.2. Mass of other components of detergent solution for 500 L tank

Abbreviation	Chemical	Role	Moles required for 2 x CMC in 500 L tank (mol)	Weight Percent (%)	Mass in 3.5 L of detergent solution (g)
LAS	Linear alkylbenzene sulfonate	Surfactant	1.6	-	556.8
MPG	Propane-1,2-diol	Hydrotrope	-	8	280
TEA	Triethanolamine	Buffer	-	4	140
Citric Acid	Citric Acid	Buffer	-	5	175

A 1 in 20 dilution of these values was used for 0.1 x CMC experiments. These values were also scaled for the stretching rig (9 L, see Section 3.3.1.1) and the rubbing rig (14.2 L, see Section 3.4.1.2). The value of the stretching rig is based on the required capacity to fully submerge the fabric without overflow. This value was then scaled by the size of the fabric for rubbing experiments.

3.1.4. Water

For all experiments, high purity reverse osmosis (RO) water was used, filtered by an Intercept Ro-S osmosis system (*ELGA Ltd*, Marlow, UK). This provided a constant level of conductance, ca. 15 $\mu\text{S.cm}^{-1}$, and water hardness below 70 mg L⁻¹ CaCO₃. The flow rig, described in Section 3.2,

requires some conductivity for flow sensors to function therefore sodium chloride would be added to give a concentration of 7.2 mM. This gives equivalent ionic strengths to hand water, allowing future comparison while removing ion effects.

3.2. Flow Rig

3.2.1. Equipment

3.2.1.1. Generation 1

Figure 3.5 shows the process flow diagram for the flow rig including the tank and flow cell. Prior to experiments, the feed solution is stored in a 500 L tank, sufficient for a 30 minute experiment without recycle, attached to a centrifugal pump. The tank contains both heating and cooling elements, and an overhead mixer. The system contains both a pump bypass (Vbp) and system bypass (Vsb) to prevent over pressures. There is also a chamber bypass, controlled by Vcb1-3, although this is rarely used and Vcb1 and Vcb3 are often open. During experiments, inlet valve Vfc1 is opened to allow the solution to enter the flow cell. If outlet valve Vcf3 is open and outlet valve Vfc4 is closed this creates cross flow, whereas the reverse creates through flow. The chamber has only been used with Vs acting as an outlet, although it is possible to use this as an inlet to create flow up through the fabric.

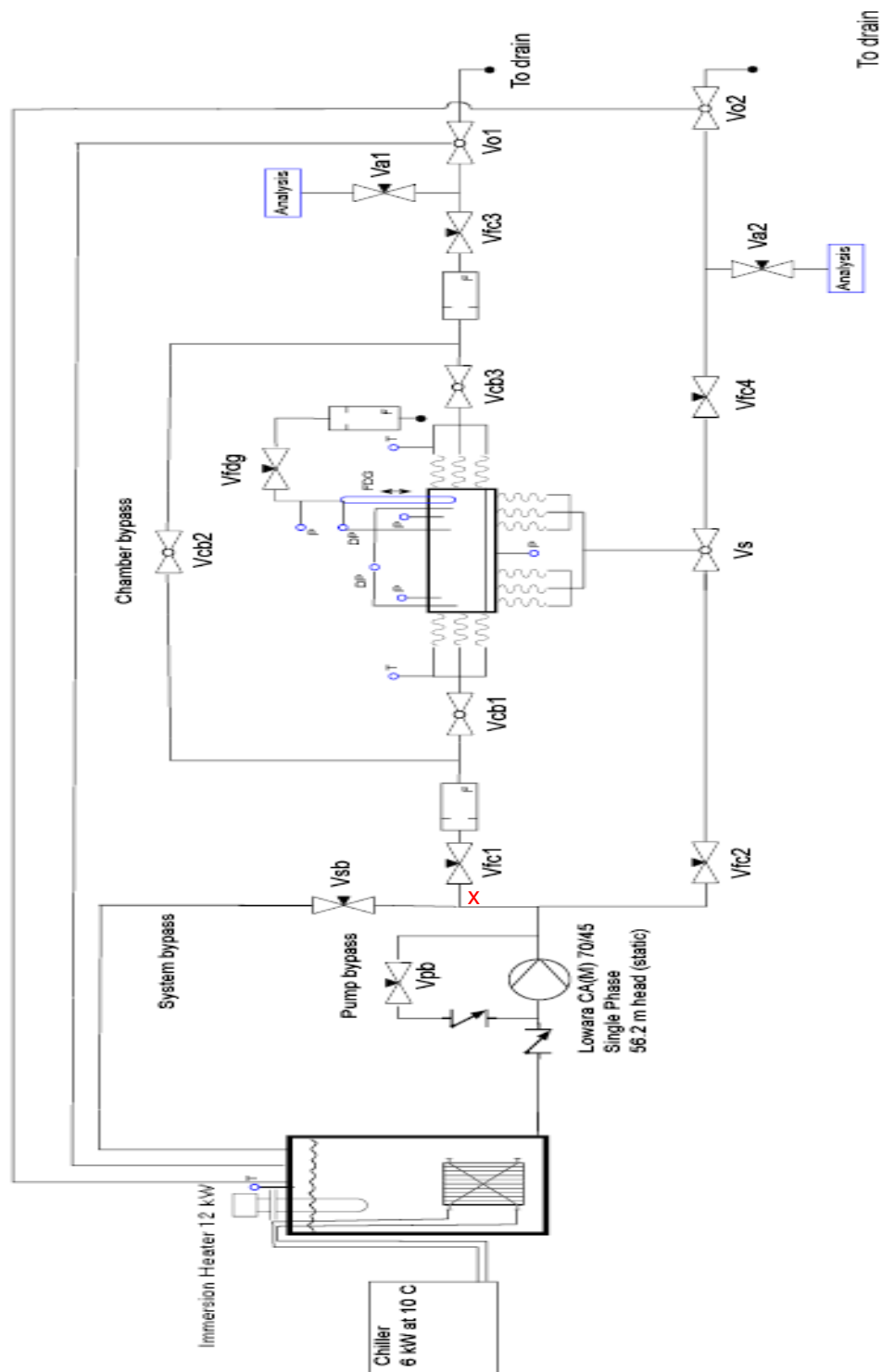


Figure 3.5. Process flow diagram for the flow rig attached to the 500 L tank. The system contains a pump bypass (Vpb) and system bypass (Vsb). The chamber bypass is controlled by valves Vcb1-3. During flow experiments Vfc1 is opened. If outlet valve Vfc3 is open and outlet valve Vfc4 is closed this creates cross flow, whereas the reverse creates through flow. Vs is currently only used as an inlet. After Muir (2012a).

Figure 3.6 shows (a) an image of the flow cell and (b) a schematic of the flow cell. When using the rig, firstly a metal grate and piece of rubber are placed in the bottom of the polycarbonate cell followed by the fabric. Another piece of rubber is placed above the fabric followed by an additional metal grate. The metal grates create a single channel 1 cm in width down the centre of the fabric giving a total test area of 35.5 cm². The polycarbonate lid is then placed on top of bolts facing upwards from the base and wing nuts are used to secure this in place. A mechanical drawing of the flow rig is included in Appendix C1.

The flow cell contains magnetic induction flow meters (*Omega Engineering Ltd*, FMG72), type ‘T’ thermocouples and gauge and differential pressure sensors (*Honeywell*, SSCDANT015PGAA3/26PCCFA6D). Pressure sensors allow calculation of hydraulic resistance changes during an experiment. A data acquisition (DAQ) device (*National Instruments*, NI-USB 6001) was used to log sensor information to a MATLAB interface.

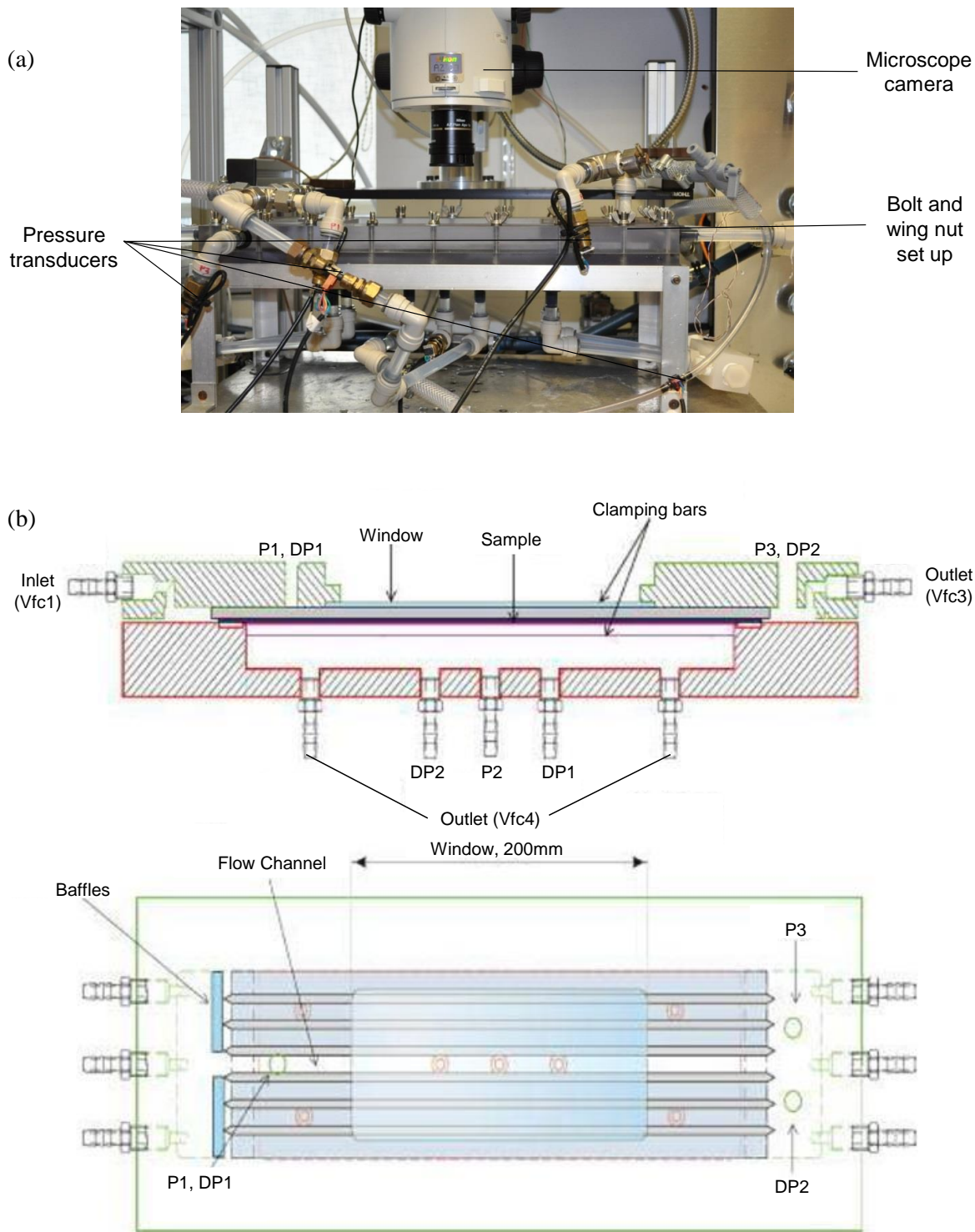


Figure 3.6. (a) Image and (b) schematic of flow rig. Wash solution enters through inlet valve Vfc1 and baffles ensure flow is directed to the middle channel only. Outlet Vfc3 is opened for cross flow and Vfc4 is used for through flow. Differential pressures (DP1-2) and gauge pressures (P1-3) are used to measure pressures. Adapted from Muir (2012b)

3.2.1.2. Generation 2

It was found that when performing flow experiments involving recycling of water, deposits were formed on the fabric. Although every effort was made to fully clean the tank and pipe work some unwanted matter remained. This is in part due to the dead volume, approximately 1 cm at the base of the tank, and in part due to the large amount of pipework connecting the tank to the chamber. To combat this a water filter (*Pentair Water*, SH247061) was added before the chamber to remove unwanted matter from the water flow. The position of the filter is shown as a red cross on Figure 3.5.

The chamber itself was also redesigned, as shown in Figure 3.7. The internal area of the chamber remained the same, but the polycarbonate was replaced with more durable hard anodised aluminium, and the bolts and wing nuts were replaced with a hinge mechanism and two screw clasps. This allowed much faster set up and changeover of experiments. When this chamber was designed a heat exchange tube was added to prevent heat loss during experiments, however for the range of temperatures investigated in this work this was not required.

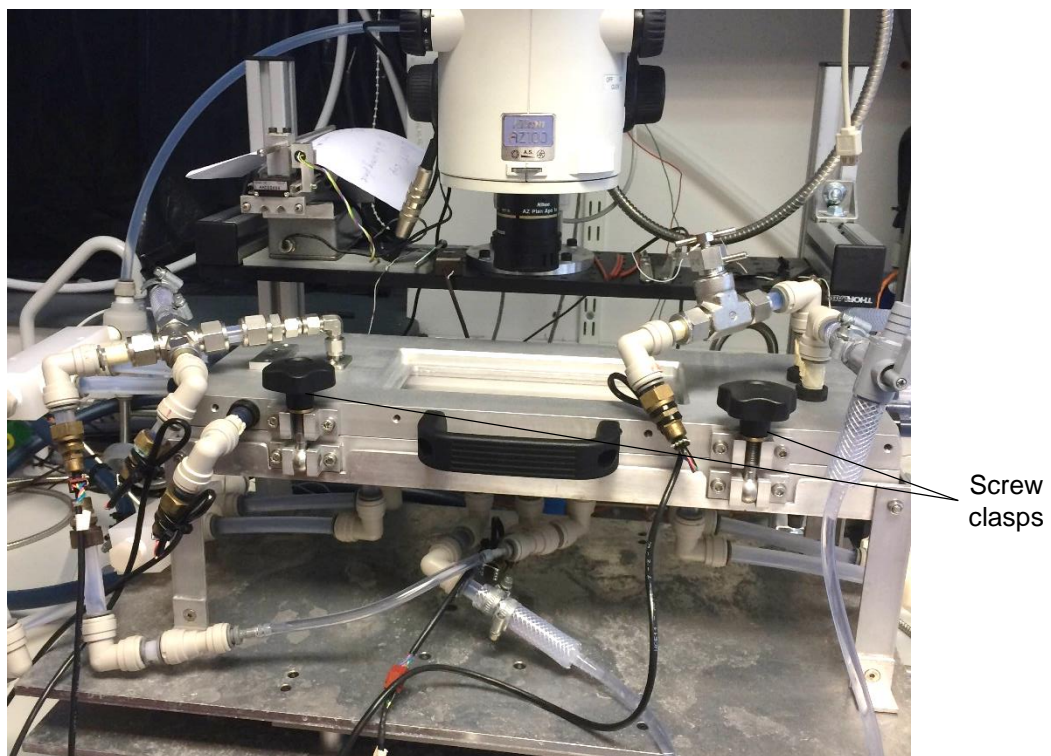


Figure 3.7. Image of flow rig generation 2 including hinge mechanism and two screw clasps.

A Fluid Dynamic Gauge (FDG) was also installed on the flow chamber to allow in situ measurements of thickness and strength of the stain. The dimensions of the gauge are $d = 4$ mm, $d_t = 1$ mm, $\alpha = 30^\circ$, $s = 0.5$ mm, as shown in Figure 2.11. The point of entry into the flow rig is sealed with an O-ring. A linear stepper assembly allowed the gauge to be moved in small graduations, and a Linear Variable Differential Transformer (LVDT) provided high accuracy measurement of gauge position. A syringe pump was used to produce the desired mass flow through the nozzle. Pressure sensors already located on the flow rig and attached to the gauge allow these properties to be quantified during an experiment. A data acquisition (DAQ) device (*National Instruments*, NI-USB 6001) was used to log sensor information to a LabVIEW interface.

3.2.2. Methods

The flow rig chamber was filled with water to the level of the fabric to prevent bubbles forming under the fabric. The soiled fabric was loaded into the cell as described in 3.2.1.1. The cell lid was then secured and the pressure sensors, temperature sensors and inlet and outlet valves attached. Cleaning solution was introduced from the 500 L tank into the cell with a flow rate of 2-3 L.min⁻¹ and air purged from the sensor lines. The chamber was then rotated to approximately 45° to remove any other bubbles. The desired flow rate and flow regime were then set and the experiment performed for between 10 and 30 minutes. The first set of results presented investigating the effect of flow with water were performed in the prototype flow cell made from polycarbonate with a bolt and wing nut arrangement, whereas testing with surfactant was performed in the new aluminum flow cell. Cleaning experiments were performed in triplicate.

At the end of the experiment the area that had been tested was marked and the fabric was removed and dried in the fume hood.

3.2.3. Cleaning the flow rig

Initially extensive cleaning of the flow rig was required to remove sebum from the tank and pipework. This was done with sodium hydroxide followed by many rinse cycles while monitoring the pH of this solution. After the introduction of the water filter and a decision to run the rig on a once through basis, cleaning only involved flushing the tank and pipework with large amounts of RO water, which removed the surfactant solution. The issue of the dead volume in the tank was resolved by flushing with RO water while concurrently draining the tank. This was done for several hours to ensure as much surfactant solution as possible had been removed.

3.3. Stretching Rig

3.3.1. Equipment

3.3.1.1. Generation 1

The stretching rig, as seen in Figure 3.8, comprises of a mechanical arm that stretches fabric horizontally. This arm is attached at an offset position on a rotating cam to transform rotary motion in to reciprocating linear motion. The offset position on the rotating cam can be adjusted to alter the length of stretch.. The arm also includes a load cell allowing quantification of the force applied, and a data acquisition (DAQ) device (*National Instruments*, NI-USB 6001) was used to log load cell data to a LabVIEW interface. A mechanical drawing of the stretching rig is included in Appendix C2. During cleaning experiments the tank is filled with 9 L of cleaning solution. The force applied to the fabric can be adjusted by a fly wheel, and the frequency of stretching can be controlled.

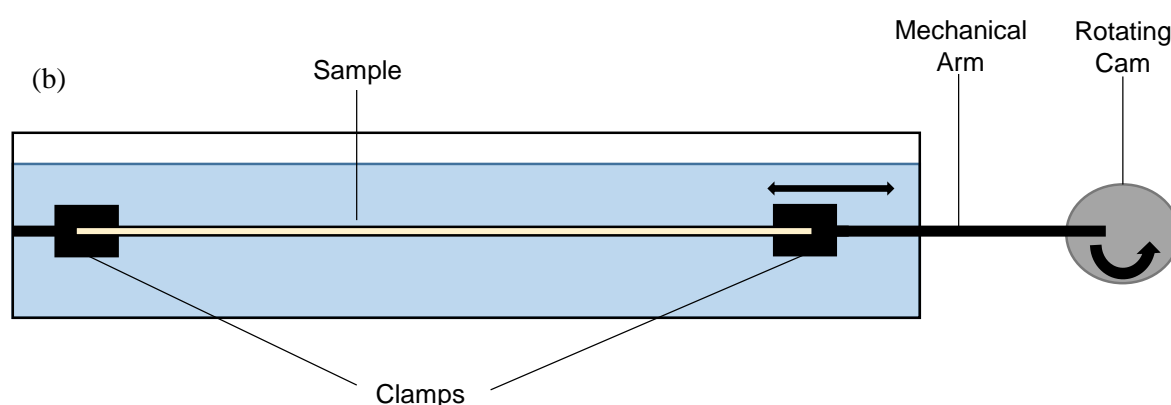
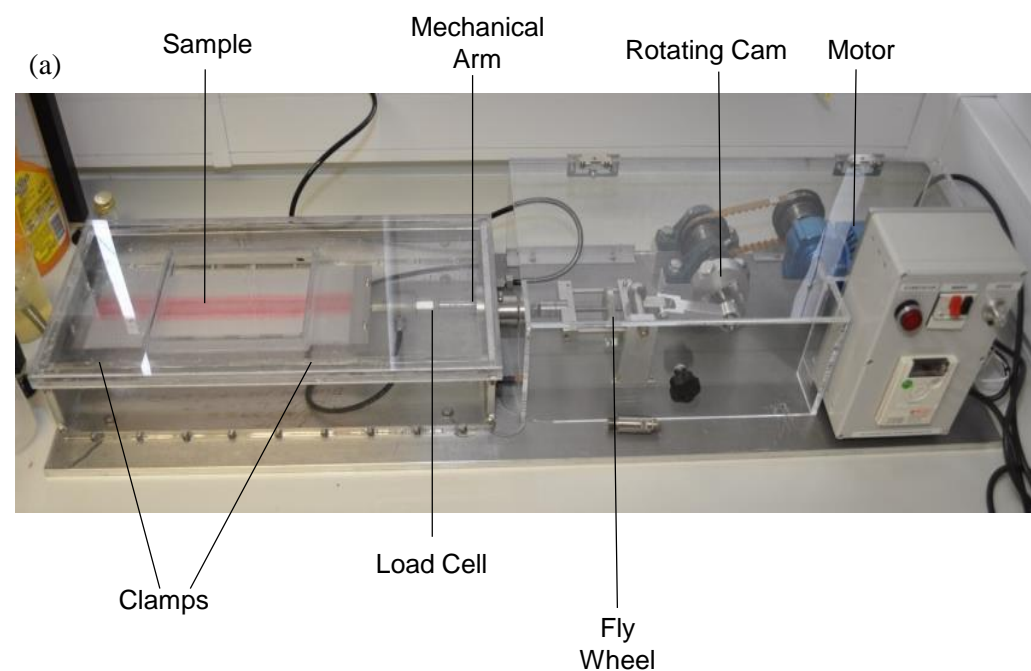


Figure 3.8 (a) Image and (b) schematic of stretching rig.

3.3.1.2. Modifications

It was found that when using the stretching rig temperature loss was an issue. For example, during a 40 °C experiment on the stretching rig the temperature would drop by up to 8 °C, which would then affect the results. To prevent this, a heat exchange was established between the tank and a metal tube connected to water bath and circulator. The optimum temperature to set this water bath to was found to be 45 °C when water or surfactant solution was added at 40 °C, and 72 °C for 60 °C experiments.

A second modification was made to the stretching rig consisting of a tensioning roller, as it was found that the rig was unable to sufficiently stretch the elastic like polyester. The fabric was placed over the roller and a metal bar placed into the crevice sandwiching the fabric in place. The roller was then turned to the desired degree of tension, which differed for the two fabrics due to their different elasticities, with a ratchet mechanism preventing it from unwinding. To achieve the desired tension, polyester was found to require about 1.5 turns, although the exact amount was determined by the tension measured with the load cell. Smaller adjustments could still be made using the fly wheel. As the cotton is thicker than the polyester, a thinner metal bar was needed. Since the cotton was not looped around the roller due to its limited elasticity, cable ties were required to prevent the force of the stretch pulling the metal bar out of the crevice and releasing the fabric. The tensioning wheel was added to the left side wall of the rig, as shown in Figure 3.9. A technical drawing of the tensioning wheel can be found in Appendix C3.

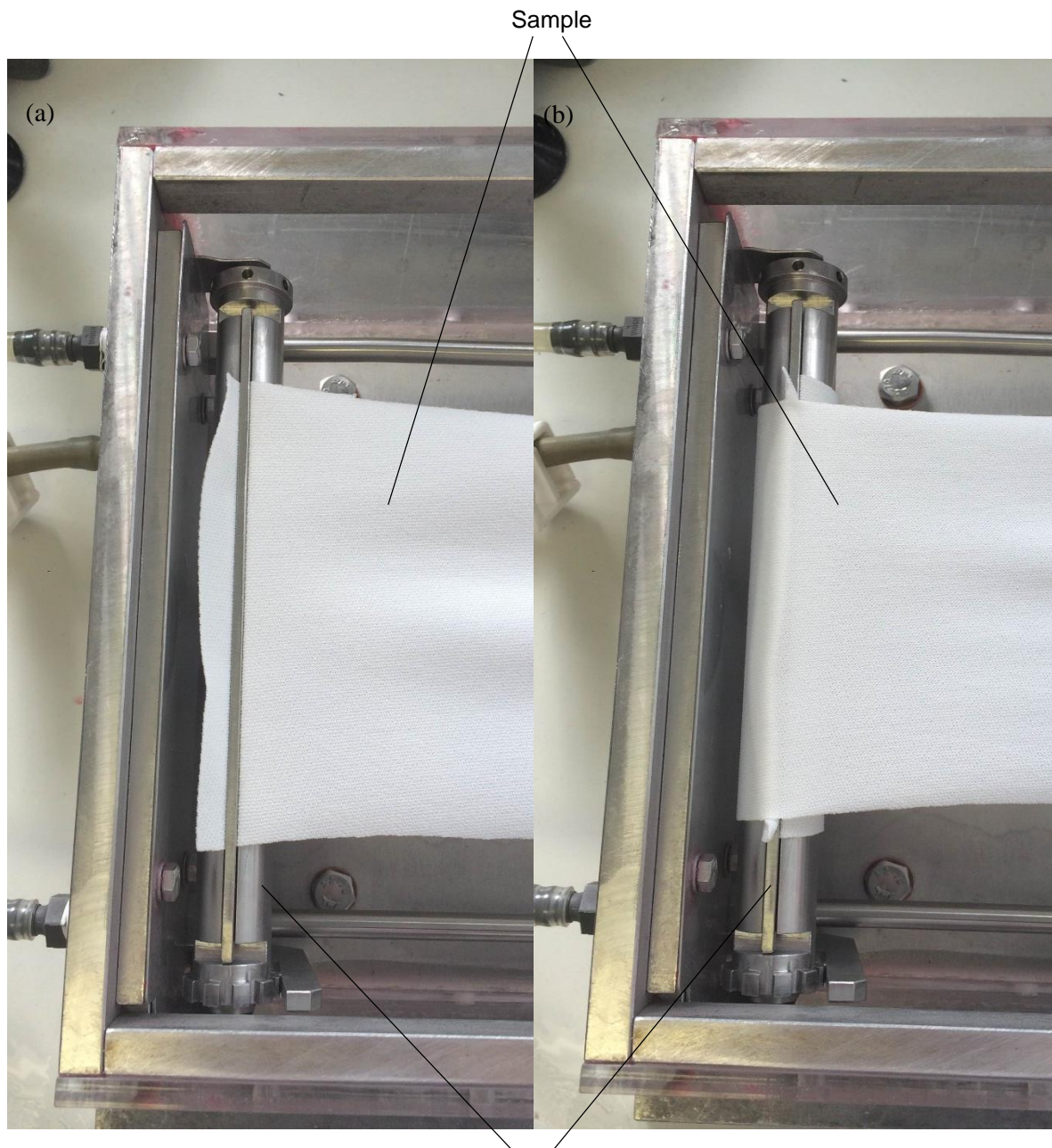


Figure 3.9. Images of tensioning wheel in the stretching rig, (a) shows the fabric clamped in place and (b) shows the fabric after it has been tensioned by wrapping around the wheel.

3.3.1.3. Calibration

The load cell on the Stretching Rig was calibrated by removing the load cell from the arm and suspending it vertically with a clamp stand. A hook and platform were then added and the change in voltage measured. Weights were then added and the force and voltage measurements plotted to give a calibration graph, Figure 3.10, which was used in future experiments. The offset from the origin

indicates the resting voltage of the load cell. The difference between vertical resting voltage and horizontal resting voltage was also measured and accounted for in the calibration.

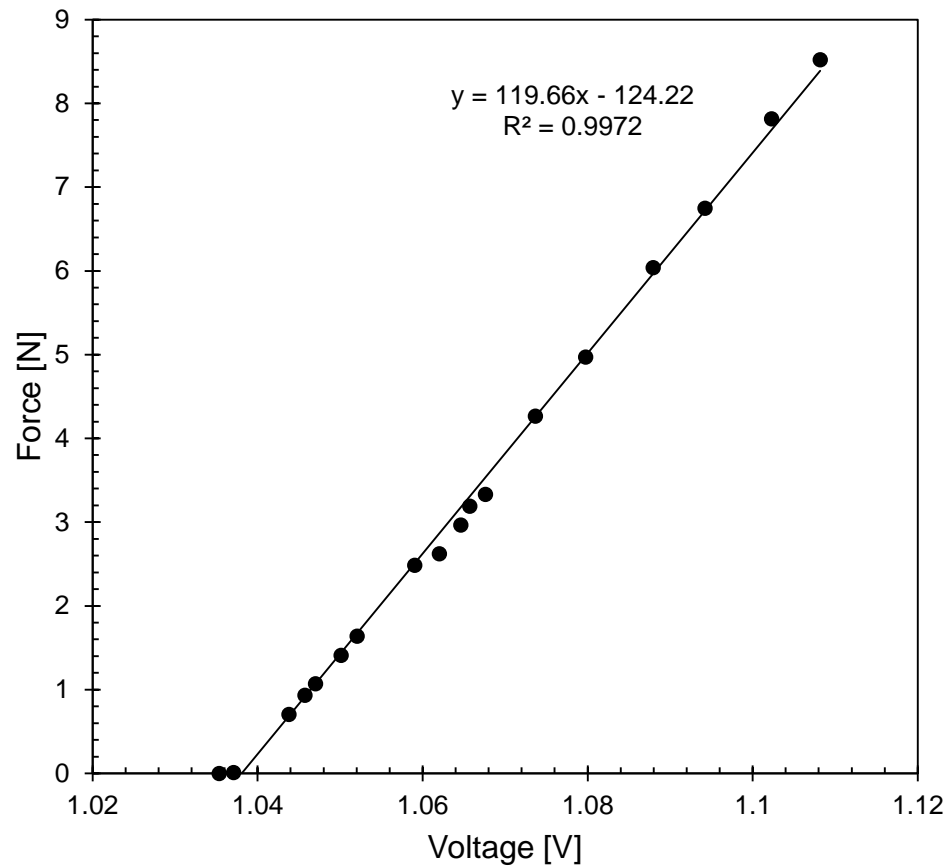


Figure 3.10. Calibration of stretching rig load cell.

3.3.2. Methods

The fabric was fitted between two clamps and the cell filled with washing solution. Both hand washing and machine washing conditions were considered and it was decided that 100 stretches over a ten minute time period would be sufficient. It was estimated that 100 stretches is the correct magnitude, and would be somewhere between the number of stretches a person would do and the number of stretches a fabric would be subject to in a washing machine. Ten minutes was chosen as a fabric may be hand washed for 1 minute (not including rinsing), whereas machine washing can take in excess of one hour, therefore 10 minutes was chosen as a compromise. A force of 10 N was initially chosen as the stretching force as it was estimated that this was the correct magnitude, with a

distance of 0.5 cm to prevent the fabric being in negative tension. However, removal was low under these conditions but due to the different elasticities of the fabrics it was not possible to increase one or both of these equally for both fabrics so different conditions were used. For polyester the 10 N force was used, but the distance was increased to 2 cm. For cotton the distance remained at 0.5 cm, but the force used was increase to 40 N. These values were chosen as some removal was seen, and the two sets of conditions involved the same amount of work done, since work is equivalent to force multiplied by distance. Fabrics were soaked in the wash solution for ten minutes prior to stretching while the fabric was clamped in place and load cell was calibrated. Stretched with then performed for ten minutes, giving a total experiment time of twenty minutes. Three fabrics were tested under each set of wash conditions.

The stretching rig was also used to investigate the effect of chemical action alone by soaking fabrics. Fabrics were soaked for twenty minutes to match the total time of other experiments. Fabrics were clamped into the stretching rig to ensure the entire fabric was submerged, and was not touching the heat exchange bar at the bottom of the tank. The fabric was not tensioned. Experiments were performed in triplicate.

3.4. Rubbing Rig

3.4.1. Equipment

3.4.1.1. Generation 1

The original rubbing rig, as seen in Figure 3.11, consists of two mechanical arms connected by a piston that pull a fabric across a smooth steel blade and around a spring loaded roller to maintain tension when the fabric stretches. During cleaning experiments, the tank was filled with cleaning solution and the rate of rubbing can be controlled.

When using the rubbing rig it was observed that only a quarter of the fabric made contact with the rubbing blade. This would make the area available for mass and colour analysis very small. It was decided that this rig was not fit for purpose, and modifications to the existing rig would not be a cost effective solution.

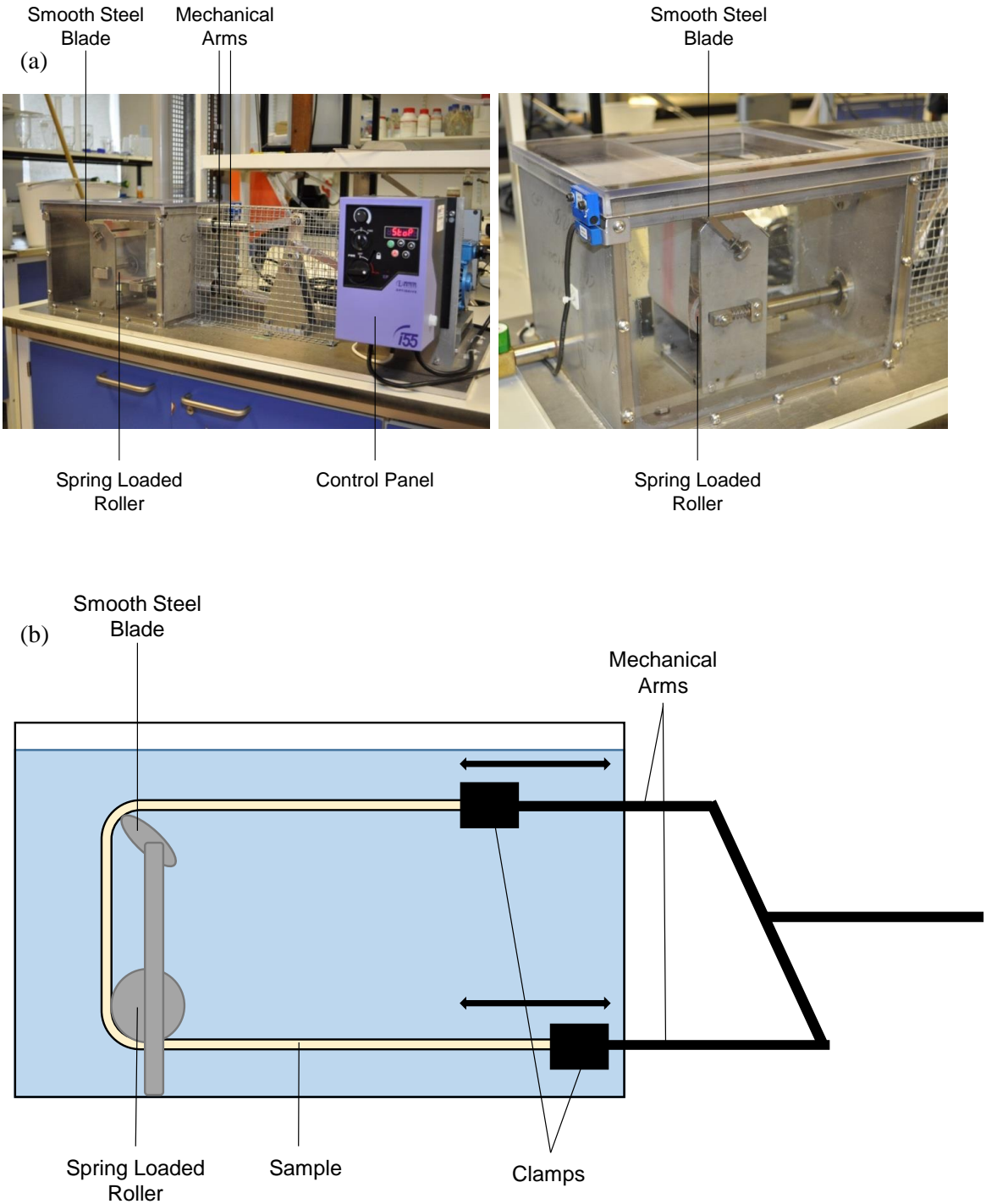


Figure 3.11. (a) Image and (b) schematic of generation 1 rubbing rig.

3.4.1.2. Generation 2

The new rubbing rig, as shown in Figure 3.12, consists of a mechanical arm that stretches fabric horizontally over a platform and a smooth steel blade attached to a motor that runs over the surface of the fabric. The arm also includes a load cell allowing quantification of the force applied to stretch the fabric, which can be adjusted with a fly wheel, and a data acquisition (DAQ) device (*National Instruments*, NI-USB 6001) was used to log load cell data to a LabVIEW interface. The tension in the spring loaded blade can be controlled by adjusting the height below the level of the fabric that the blade begins at, and the frequency of rubbing can be controlled. The blade could be a smooth metal edge, or fabric could be attached to give a fabric-to-fabric rub. During cleaning experiments the tank is filled with 14.2 L of cleaning solution. This allows the same volume of water per unit area of fabric as the stretching rig, since a larger area of fabric is required for use in the rubbing rig. This rubbing rig was also designed to incorporate a heat exchange coil to allow for better temperature control, which was attached to a water circulator bath. It was found that for experiments at 40 °C this needed to be set at 47 °C when 40 °C water was added to the rig, and for 60 °C experiments it need to be set at 75 °C. Two mechanical drawings of the rig, one of the front view and one of the top view, are included in Appendix C4.

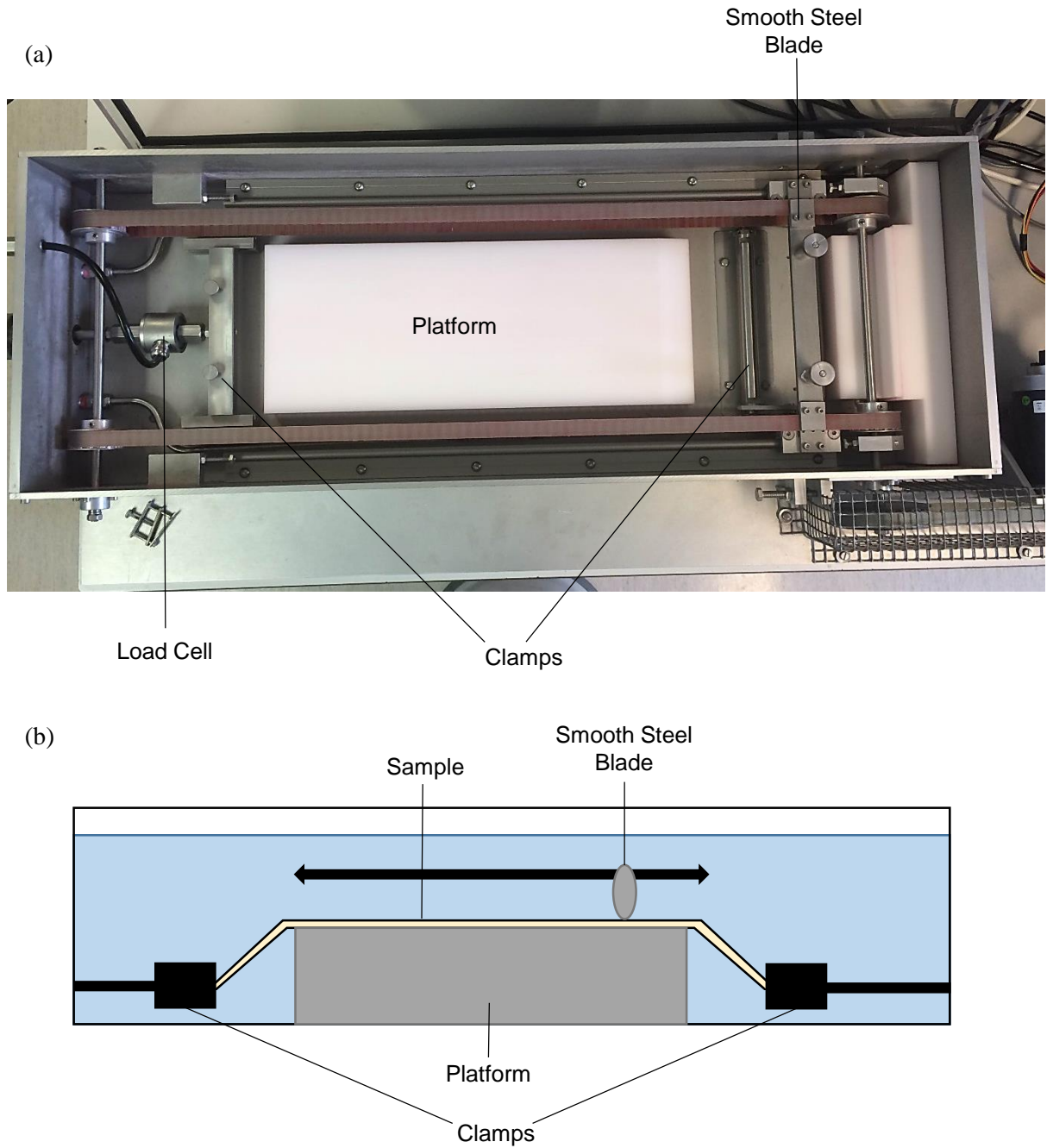


Figure 3.12. (a) Image and (b) schematic of generation 2 rubbing rig.

As with stretching experiments, it was found that polyester was not sufficiently taut during rubbing experiments and bowed as shown in Figure 3.13. A tensioning wheel was also added to this rig, this time attached to the base plate, as shown in Figure 3.14. A mechanical drawing can be found in appendix C3. This allowed the fabric to be tensioned before rubbing preventing bowing and producing a more even rub. The fly wheel was used for smaller adjustments in tensioning.

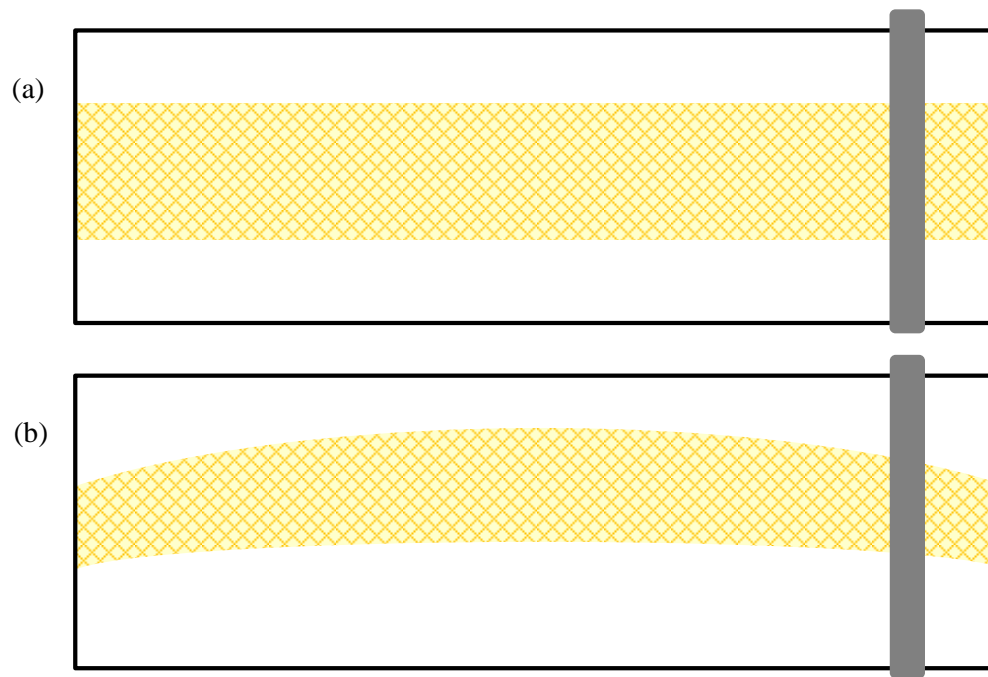


Figure 3.13. Diagram of (a) sufficiently taut fabric and (b) fabric bowing due to being loose

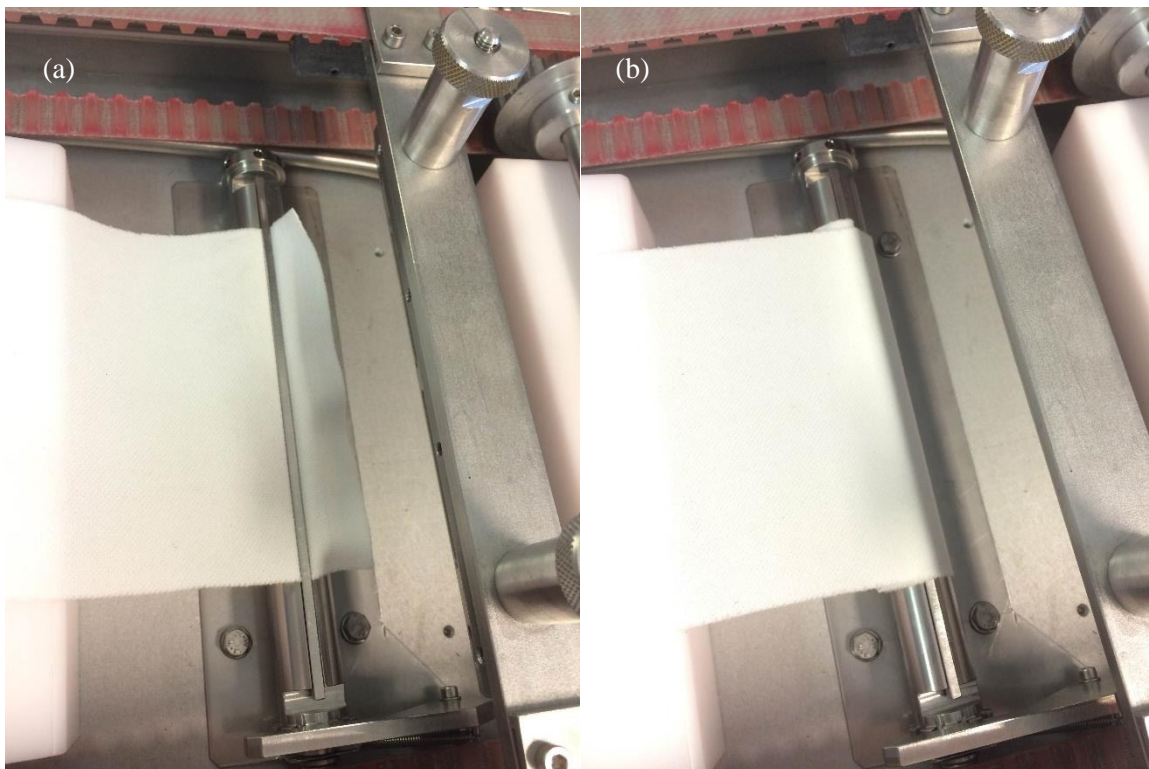


Figure 3.14. Images of tensioning wheel in the rubbing rig, (a) shows the fabric clamped in place and (b) shows the fabric after it has been tensioned by wrapping around the wheel.

3.4.1.3. Calibration

The load cell on the Rubbing Rig was calibrated by removing the load cell from the rig and suspending weights from it. A range of weights were tested and the average voltage reading from the load cell was taken over a thirty second time period. The voltage and force readings were then plotted to give a calibration plot, Figure 3.15, which was used in future experiments. As with the stretching rig, the offset from the origin indicates the resting voltage of the load cell. The difference between vertical resting voltage and horizontal resting voltage was also measured and accounted for in the calibration.

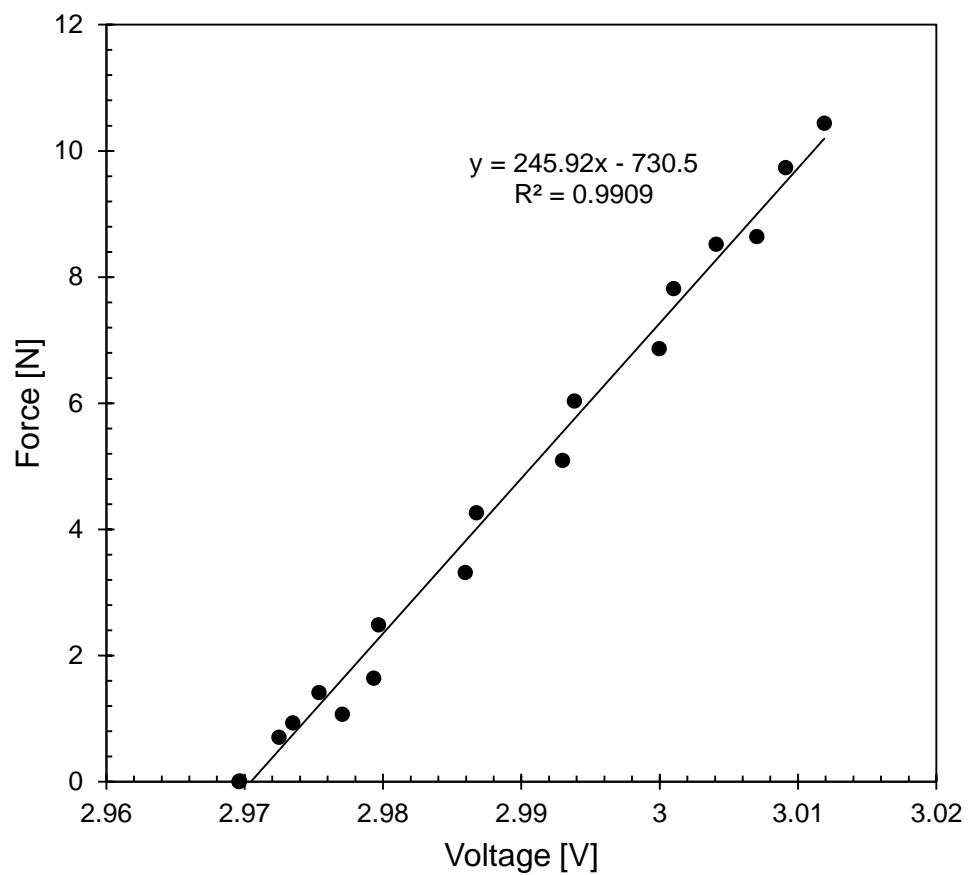


Figure 3.15. Calibration of rubbing rig load cell.

3.4.2. Methods

All results reported in this thesis used the Second Generation rubbing rig. The cell was then filled with washing solution taking care to achieve the correct temperature. The fabric was then placed on the platform and stretched to 5 N between two clamps, then the rubbing blade moved over the fabric. The rubbing blade contained 2 springs that compressed when on the platform providing the downward force on the fabric. To determine the force exerted on the fabric by the blade calibration of the springs was required to find the force constant, k . The springs were loaded with various weights and the extension recorded, as shown in Figure 3.16. The gradient gives the force constant of each spring. Since the springs are loaded in parallel they act as a single spring, where the force constant equals the sum of the force constants of the two individual springs, therefore k was found to be 2.87 N.mm^{-1} . It was decided that the full extension of the spring, 5 mm, would be used giving a downward force of 14.35 N for 100 rubs. Fabrics were soaked in the wash solution for ten minutes while the fabric was clamped in place and the load cell was calibrated. Fabrics were then rubbed for ten minutes, giving a total experiment time of twenty minutes. Experiments were performed in triplicate.

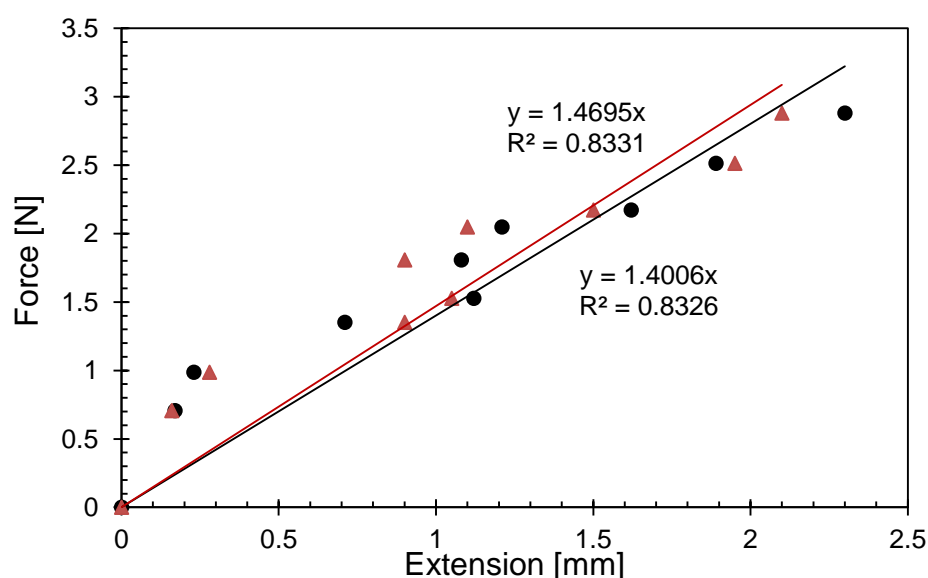


Figure 3.16. Calibration of the springs in the rubbing rig blade

3.5. Analytical Techniques

3.5.1. Measurement of Mass

3.5.1.1. Method 1

Cleaned samples were imaged using a camera (*Nikon*, Coolpix L310) in three different orientations. Fabrics were then weighed on an analytical balance (*Adam Equipment*, PW254) and the mass recorded by a data logging computer. They were placed on pre-heated adapted hot plate which allowed the whole sample to lie flat. The fabric was heated at 115 °C for 15 minutes before reweighing. Three further masses were recorded at 5 minute intervals while heating in an attempt to remove the effects of humidity. Reweighing produced a curve as the sample absorbed moisture from the air after removal from the hotplate. A MATLAB script was used to fit curves to the three mass curves to find the average mass of the cleaned cloth.

For samples from the flow rig the marked strip was cut from the bulk fabric and only that area was weighed. Together with the total cloth area found from imaging the sample and the initial mass per unit area measurement, the mass measurements could be used to give the percentage ratio change in mass of soil per unit area.

However due to the number of steps used in this method it was found to have very high errors based on both mass and area values. This can be seen in Appendix B. It was also suspected that heating the sample to 115 °C may affect the results.

3.5.1.2. Method 2

Samples were stored in the fume hood prior to mass measurement. A four decimal place balance (*Adam Equipment*, PW254), also stored in the fume hood, was used to measure mass. Results were reported as percentage improvement to allow meaningful comparison between mass, colour and resistance measurements. This method gives a more crude mass result, but has significantly less

associated error and didn't involve heating the fabrics therefore was used in most of this work. Three samples were prepared and measured to give meaningful results.

Of interest also was the location of the soil after cleaning, in particular whether the soil that remained on the fabric had remained within the area of the soil strip or spread out over the fabric, as shown in Figure 3.17.



Figure 3.17. Schematic of spread of soil on surface of fabric.

To measure this strips of approximately 15 cm² were cut and the mass measured as described in method 2. The area was measured as described in method 1 and results combined to give a mass per area measurement. This was done for 9 strips down the length of each fabric, and three repeats were measured for each set of washing conditions to give statistically significant results. A diagram of the fabric with the soiled area highlighted in red is included above each graph.

3.5.2. Measurement of Colour

Sebum was dyed red to allow colour to be used as a proxy for mass removal, although it is important in its own right as a consumer will often judge cleanliness of an item by sight. The colour of the stained fabric was measured at five points along the strip of sebum, against the white tile standard, by a Spectrophotometer (*Datacolour*, Spectraflash 600 PLUS) to give average L*, a* and b* measurements. D65 light was selected for testing as it is a commonly used standard illuminant and emulates midday light in Europe. This was repeated after cleaning tests and the difference between the two averaged results was reported as a percentage improvement.

During experiments soil could be removed, but could also be pushed through the fabric and remain on the other side, which would show an improvement in colour without loss of sebum, as shown in Figure 3.18. Therefore it was decided that for some experiments both topside and underside measurements of colour were recorded to investigate the effect on both sides of the fabric.

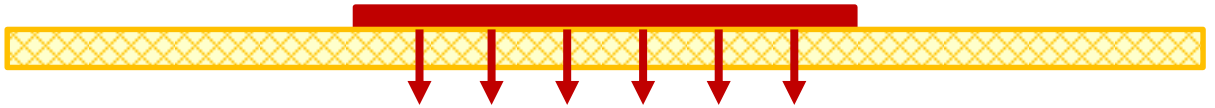


Figure 3.18. Schematic of soil permeating the fabric.

3.5.3. Measurement of Resistance

A dead end filtration set up was used to measure resistance. Both the mass of water that passed through the fabric and the time taken for this were recorded by a LabVIEW interface. This was repeated with five different areas of fabric from the same sample to give an average. The resistance of the fabric alone was also calculated and subtracted from that of stained or cleaned fabric results to give just the resistance of the sebum alone. The difference between the stained and cleaned fabrics gave a resistance change due to cleaning as a percentage to allow comparison with colour and mass. Further details of this method including equations used to calculate resistance can be found in Appendix A.

3.5.4. Fluid Dynamic Gauging

Figure 3.19 shows the static FDG apparatus used for strength tests. Static indicates that the experiment is not under flow conditions. The FDG nozzle is normal to the surface and the syringe pump maintains a constant mass flow rate through the nozzle. The proximity to the surface affects the pressure reading from the pressure transducer, which in turn gives an indication of the height of the nozzle above the surface.

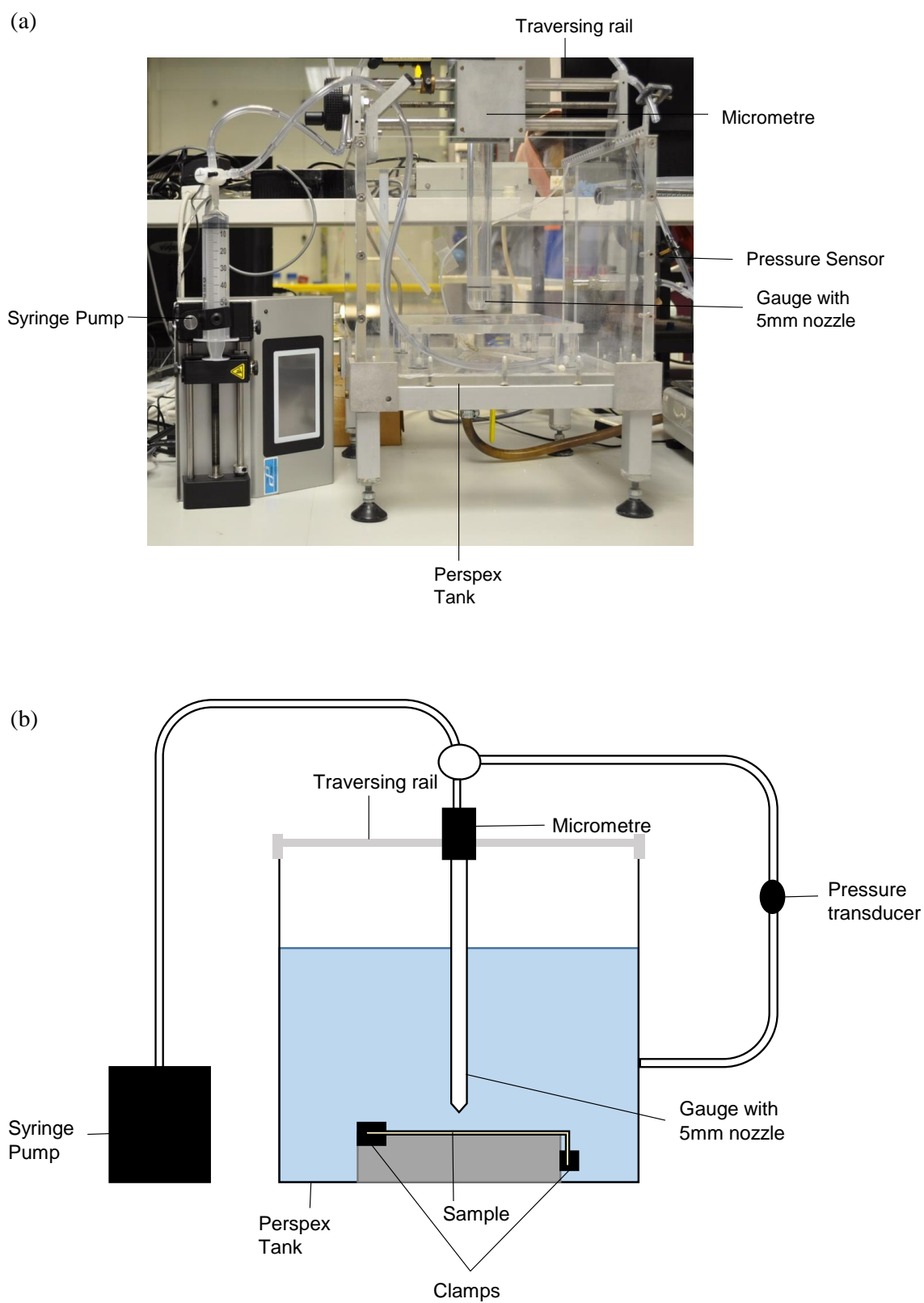


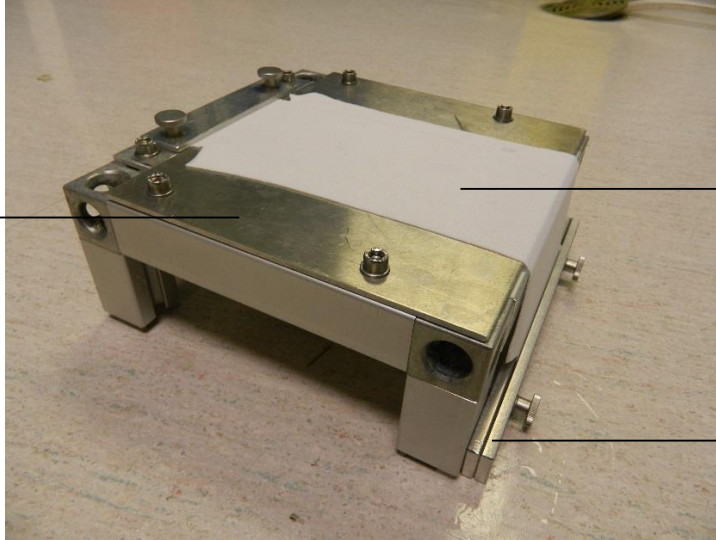
Figure 3.19. a) Image and b) schematic of static FDG

Apparatus of the following dimensions was used in these experiments (see Figure 2.11) $d = 25$ mm, $d_t = 5$ mm, $\alpha = 30^\circ$, $s = 5$ mm. This nozzle is able to apply shear stresses in the range of 2-30 Pa. Prior to testing, samples were imaged by a mono-zoom optical microscope (*Nikon*, AZ-100 Multizoom) attached to a colour digital CCD camera (*Basler*, Aviator avA2330-25gc) and by a Spectrophotometer (*Datacolour*, Spectraflash 600 PLUS). Samples were then placed under the nozzle at various h/d_t values to apply a range of stresses. Samples were imaged at the gauged point after testing to compare surface coverage and colour change.

Heat loss was also found to be an issue when using the FDG, so a heat exchange coil was also added to this rig to ensure consistent temperature throughout experiments. For 40 °C experiments it was found that setting the water at 44 °C was sufficient to maintain this temperature, and a temperature of 72 °C was required for experiments performed at 60 °C. The syringe pump was replaced with a gear pump and flow meter set up, which allowed higher mass flow rates through the nozzle giving higher shear stresses. However, this caused an issue in that the force was so strong the fabric was pulled towards the nozzle during testing. For this reason it was necessary to construct a tensioning platform for the fabric, which is shown in Figure 3.20. For some experiments, additional masses were added to the sides of the fabric, totaling 1125 g.

(a)

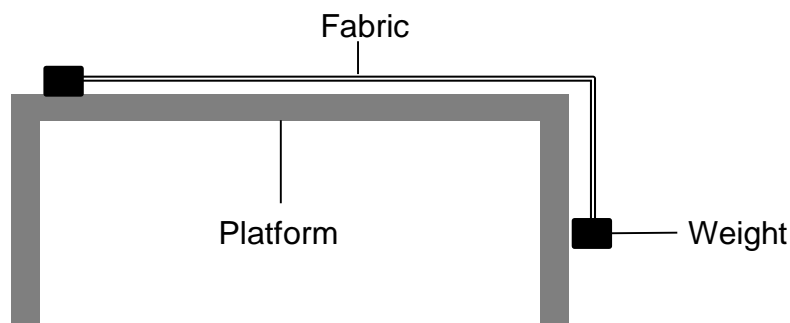
Platform



Fabric

Weight

(b)



Fabric

Platform

Weight

Figure 3.20. (a) Image and (b) schematic of tensioning platform for fabric during FDG tests.

Two additional nozzles were also constructed with dimensions shown in Figure 2.12. These nozzles contained angles of $\beta = 5^\circ$ and $\beta = 15^\circ$ which maximised shear stress and normal force, respectively.

3.5.5. Fabric Drying Time Test

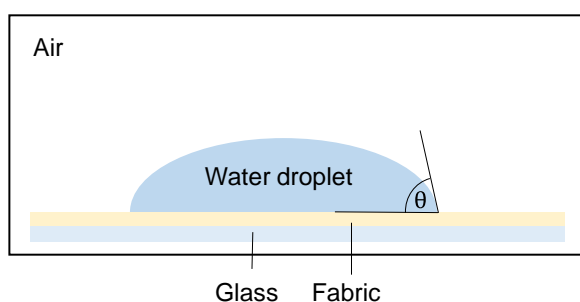
The amount of time it takes to dry a piece of fabric after testing is of interest as it informs when analysis can begin. Fabric was soaked in 20 °C water for ten minutes and left to dry on a washing line in a fume hood. It was then measured on a balance (*Adam Equipment*, PW254) inside the fume hood every ten minutes until a constant mass was reached.

3.5.6. Contact Angle Measurements

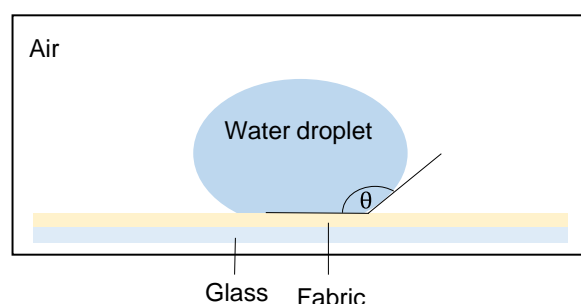
Comparison of contact angle measurements gives information on the wettability of different surfaces, which in turn gives information about the hydrophobicity. Using the sessile drop method a hydrophobic surface will have a contact angle greater than 90° and a hydrophilic surface will have a contact angle less than 90° , whereas using the captive bubble method this is reversed, as shown in Figure 3.21 below.

Sessile Drop Method

More hydrophilic

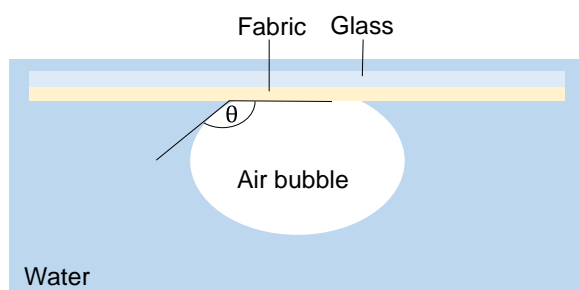


More hydrophobic



Captive Bubble Method

More hydrophilic



More hydrophobic

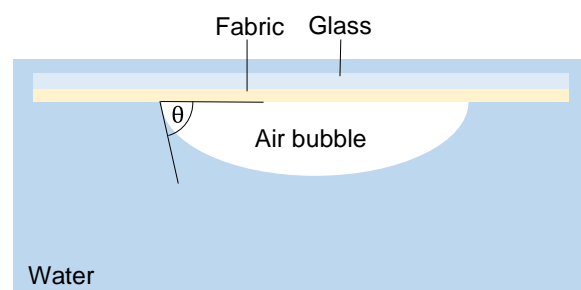


Figure 3.21. Schematic diagram showing sessile drop and captive bubble contact angle measurements.

For the sessile drop method a horizontal stage was used to mount a piece of fabric attached to a microscope slide and a drop of water was released from a micropipette. Various volumes of water were tested, as well as a more viscous liquid, sunflower oil.

For the captive bubble measurement a purpose built chamber was used that had a viewing window for the mounted fabric. A small amount of air was injected under the sample to form an air bubble at the surface. This can be seen in Figure 3.22 below.



Figure 3.22. Image of captive bubble used to find contact angles with the fabric surface at the top of the image.

For both methods the experimental set up with camera (*Dataphysics*, OCA) was used to capture the image and a computer program used to find the contact angle. Due to the uneven fabric surface each measurement was repeated at ten different points on the fabric, giving 20 contact angle values.

3.5.7. Imaging pore size, yarn width and fibre width

Fabrics were imaged using a microscope camera (*Nikon*, AZ-100 Multizoom; Basler, Aviator avA2330-25gc) and the images analysed by MATLAB. To determine the size of the pores firstly a threshold was established, and then the image was closed. Thresholding transforms the image to a black and white image by simply accepting a certain level of colour as sufficient and making that pixel white, or if it is not sufficient it becomes black. Closing involves filling in any gaps in the pores that are too small to be anything significant. The average pore size as a number of pixels was the determined and compared to a standard scale.

The size of yarns and fibres was determined using the same microscope and camera set up. The yarns were placed on a black background to give extra definition. Images were then compared to the image of a scale bar to determine the width of the fibre using MATLAB. 10 images were used to give statistically valid results.

3.5.8. Zeta Potential

The surface charge is important in cleaning fabrics, especially when surfactant molecules used in detergent are often charged. The surface charge is related to the zeta potential of the surface, which can be determined using streaming potential measurements. Streaming potential measurements can be made when an electrolyte solution flows across a surface or through the pores. For fabric, since the pores are large in size, these two effects are difficult to separate out, i.e. when does the top surface end and when does the pore begin. For through pore measurements a resistance to flow of electrolyte is required, and a single layer of fabric does not provide this, therefore multiple layers were used (between 2 and 8) but the number required depended on the fabric and the level of soil on the surface.

Measurements were carried at Lappeenranta University of Technology. Circular fabric disks of 1.3 cm diameter were cut from sheets of fabric using a sharp metal cylinder and hammer. These were then layered in between plastic disks with large holes in a plastic cylindrical tube, a set up often used for powder samples. This was then attached to an electrokinetic analyser (*Anton Paar SurPass*, Version 2.20) with Ag/AgCl electrodes. A 0.001 mol L⁻¹ KCl solution was used as electrolyte, and HCl used to drop the pH from 8 to 3 in small increments during the experiment. Four measurements were taken at each pH.

Since rubbing causes the greatest removal it was selected, as well as soaking to give a comparison with the effect of chemical action alone. Time was also limited so repetitions of all samples were not possible, therefore a couple of samples were selected to test repeatability. Figure 3.23 shows two conditions there were selected, both of which did show good repeatability.

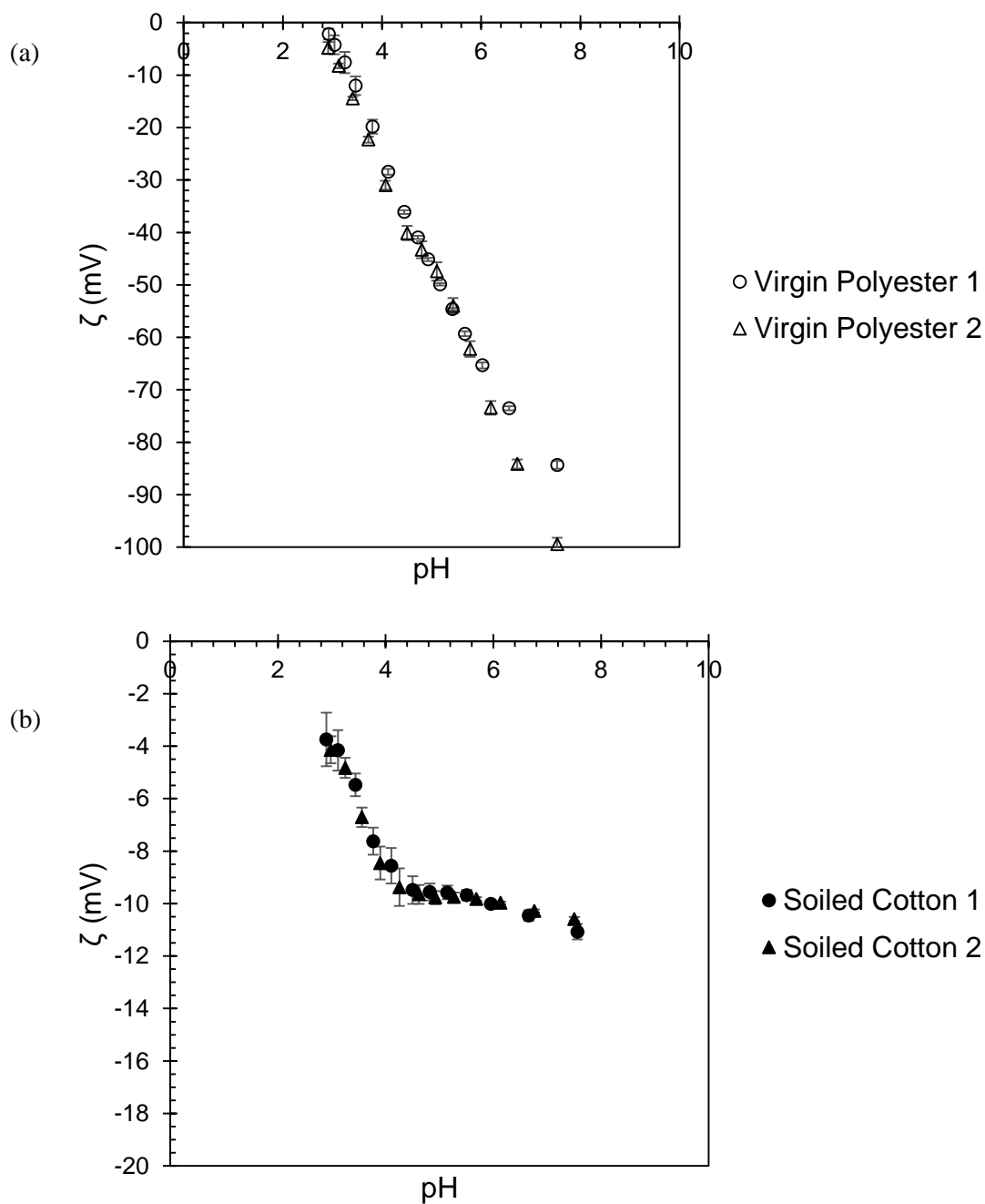


Figure 3.23. Zeta potential of (a) virgin polyester and (b) soiled cotton to test repeatability. The error bars represent \pm one standard deviation for four repeat measurements taken on each fabric.

It was also important to investigate whether the number of layers used effect the results. Figure 3.24 below shows one set of conditions, 40 °C 2 x CMC soaked polyester fabric, tested with two and four layers. No difference was found between these results so meaningful comparisons can be made between samples tested with different numbers of layers of fabric.

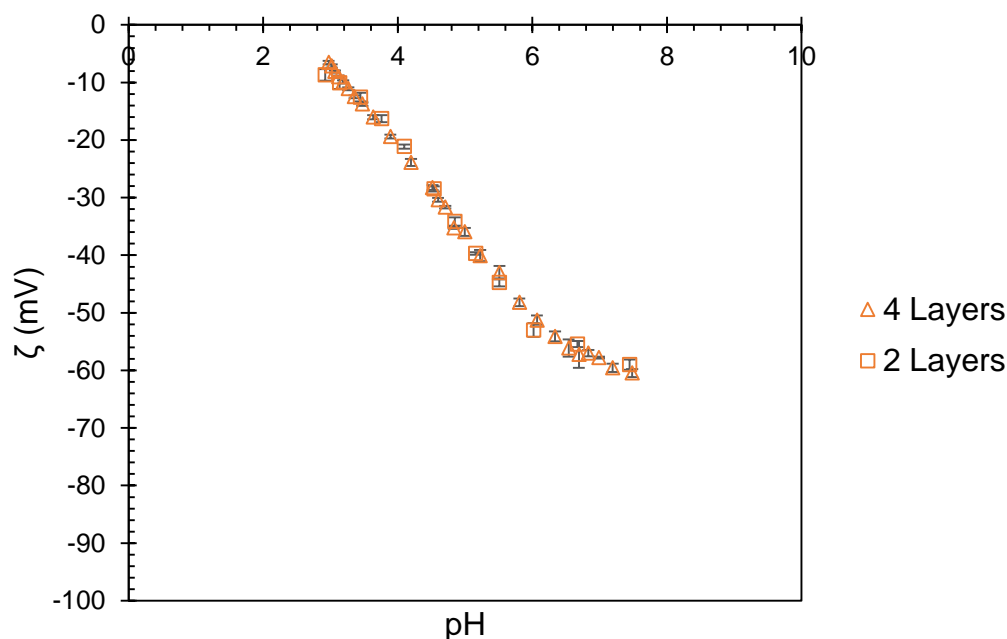


Figure 3.24. Zeta potential of 40 °C 2 x CMC soaked polyester fabric with two and four layers of fabric. The error bars represent \pm one standard deviation for four repeat measurements taken on each fabric.

3.5.9. Fourier Transform Infra-red Spectroscopy

The fabric surface was analysed using Fourier transform infra-red spectroscopy (FTIR). FTIR is a useful technique for establishing which chemical groups are present on the surface, which in turn shows whether soil has been removed. An FTIR spectrometer (*Perkin-Elmer*, Spectrum 100) measured percentage transmittance over wavenumbers from 4000 to 650 cm^{-1} . Samples were measured with 4 repeat scans in ATR mode (attenuated total reflection). The force exerted by the clamp was set to 25 force units for polyester and 50 force units for cotton. These values were used to get the best spectra without penetrating the layer of soil on the fabric. Results of fabrics cleaned using mechanical, chemical and hydrodynamic actions were compared to both virgin and fouled samples. Both the top and under surface were studied to investigate where on the fabric sebum had been removed from, and whether some of the soil had migrated through the pores to the opposite side.

3.5.10. Scanning electron microscopy

Scanning electron microscopy (SEM) was used to image fabric samples to show the morphology of the virgin, soiled and cleaned surface. Samples were prepared by placing a 1 cm² piece of fabric on to conductive carbon tape, adding a small piece of tape on top of one edge of the sample and placing in a desiccator under vacuum for 48 hours. Samples were then coated in gold for three and a half minutes under an atmosphere of argon using an *Edwards* Sputtercoater S150B and then imaged by SEM (*JEOL*, SEM6480LV). All samples were imaged at magnifications of 20, 100 and 500, and some samples were imaged at 1000 and 5000. 10kV of power was used for the filament, with a spot size of 25 and secondary electron analysis for all samples, however the working distance was varied to achieve the best images.

3.5.11. Interfacial tension measurements

Interfacial tension measurements were used to determine the Critical Micelle Concentration (CMC) of the surfactant in water. The CMC of a surfactant is the concentration at which micelles form, and above this concentration any additional surfactant molecules will become micelles. This is an important value in cleaning as the behaviour of the solution changes at this point, therefore mechanisms of cleaning also change.

To measure interfacial tension the solution was added to a glass barrel attached to a needle. This was inserted into the analysis equipment (Dataphysics, OCA) such that the needle was in line with a camera. The camera was rotated 90 ° so the drop could fill the maximum amount of the screen. 3 µL was released from the needle at a rate of 1 µLs⁻¹. The image of the droplet was then centred on the screen and a photo taken. The profile of the drop was then extracted and interfacial tension calculated.

3.5.12. Differential scanning calorimetry

Differential scanning calorimetry (DSC) was used to investigate the thermal properties of sebum, which it does by measuring the amount of heat energy required to increase the temperature of the

sample and the reference at the same rate. DSC measurements were performed at Unilever, Port Sunlight. Sebum was cooled from room temperature to -10 °C. It was then heated to 70 °C with a reference. Samples were then cooled to -10 °C and the process was repeated. Each of these measurements were performed twice.

Chapter 4: Characterisation of Fabrics, Soil and Surfactant

This chapter investigates the properties of virgin and soiled polyester and cotton, sebum and LAS surfactant. Results from this chapter are used later in this thesis for comparison to cleaned fabrics. Analytical techniques used include SEM, FTIR, zeta potential and DSC.

4.1. Fabrics

4.1.1. FTIR

FTIR is a useful analytical technique for confirming the presence of functional groups on the surface. Virgin polyester and cotton are presented here, and will be used later in this thesis for comparison with soiled and cleaned fabrics.

4.1.1.1. Polyester

Figure 4.1 shows the FTIR spectrum for virgin polyester. The functional groups of polyester can be identified in the spectrum, including the para substituted benzene ring and both the C=O and C-O bonds from the ester group, as listed in Table 4.1.

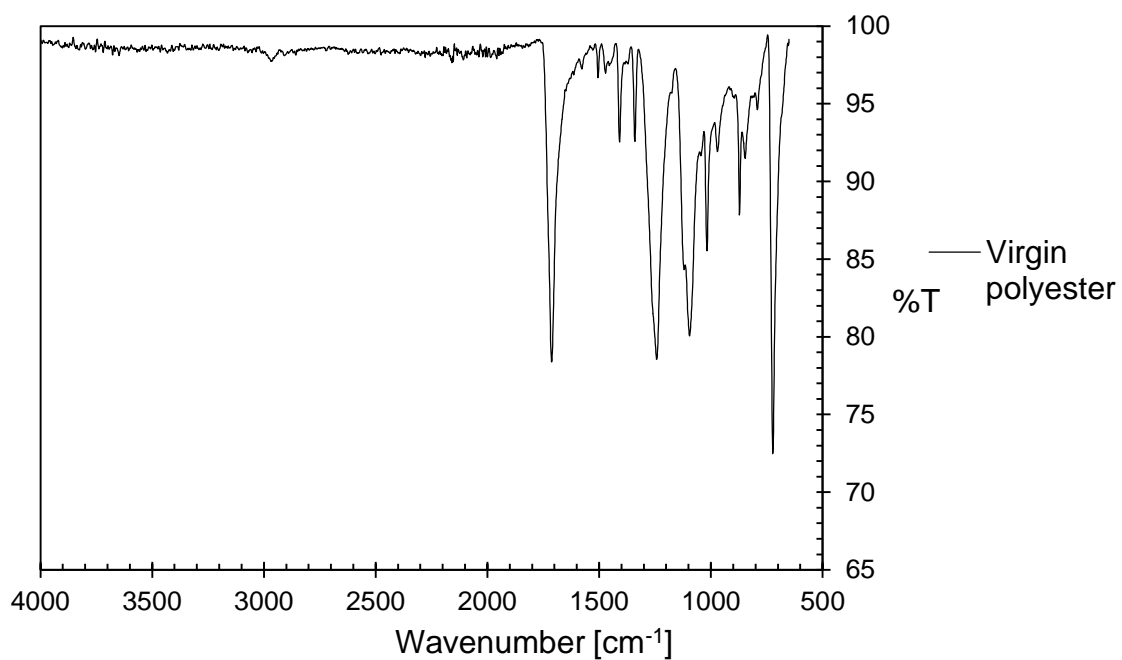


Figure 4.1. FTIR spectrum of virgin polyester.

Table 4.1. Peak table for FTIR of virgin polyester

Peak (cm ⁻¹)	%T	Assignment
1713	78.36	C=O stretch
1409	92.53	Aromatic C=C stretch
1340	92.56	CH ₂ bend
1242	78.54	C-O stretch
1095	80.05	C-O stretch
723	72.45	Aromatic C-H bend (para)

4.1.1.2. Cotton

The FTIR spectrum of virgin cotton is shown in Figure 4.2, and the peaks are listed and identified in Table 4.2. Peaks characteristic of the O-H and C-O groups of cotton can be clearly seen.

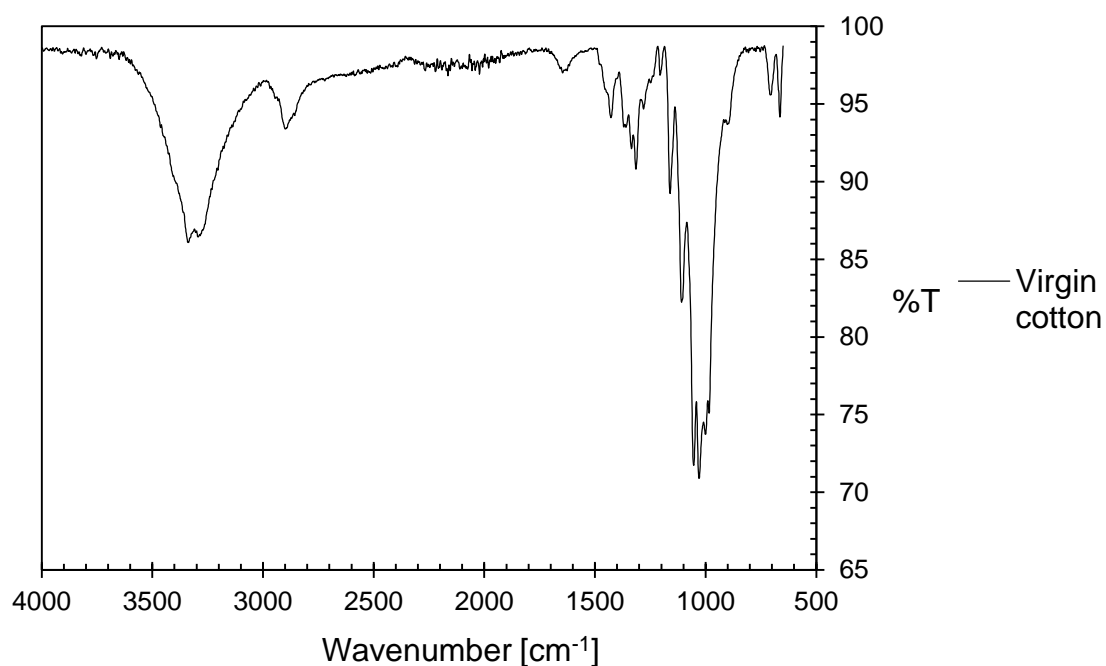


Figure 4.2. FTIR spectrum of virgin cotton.

Table 4.2. Peak table for FTIR of virgin cotton

Peak (cm ⁻¹)	%T	Assignment
3339	86.08	O-H stretch
2898	93.39	C-H stretch
1428	94.12	C-H bend
1315	90.80	CH ₂ bend
1161	89.23	-C-H bend
1190	82.23	C-O bend
1054	71.73	C-O stretch
1030	70.88	C-O stretch

4.1.2. Zeta Potential

Zeta potential gives information about the surface charge of the fabric, which will have a significant effect on soiling and cleaning. The zeta potential of virgin polyester and cotton are presented in Figure 4.3, and will be used for comparison later in this thesis. It can be seen that cotton is less

negatively charged than polyester, and neither fabric reaches its isoelectric point in this pH range. Cotton is found to have a more negative surface charge than is reported in the literature (Bellmann et al., 2005); it is suspected that this is due to modification by the detergent used to desize the fabric.

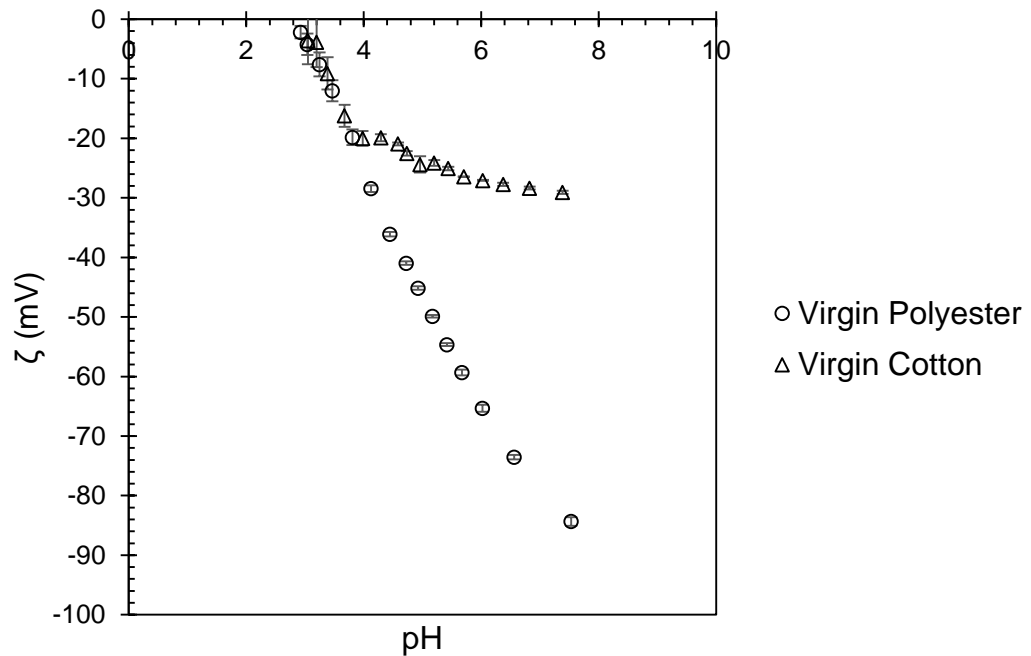


Figure 4.3. Zeta potential of virgin polyester and virgin cotton. The error bars represent \pm one standard deviation for four repeat measurements taken on each fabric.

4.1.3. SEM

4.1.3.1. Polyester

Polyester imaged with SEM (Figure 4.4) at x20 magnification show the knitted pattern of this fabric is very complicated. At x100 magnification fibres can be seen making up yarns, however the yarns are not very tightly bound and there is a lot of space in the intra yarn pores. Inter yarn pores appear smaller due to the spreading of the fibres, but are still sizable. Images at x500 and x1000 magnification show smooth spherical fibres without many imperfections, as expected with synthetic fabrics.

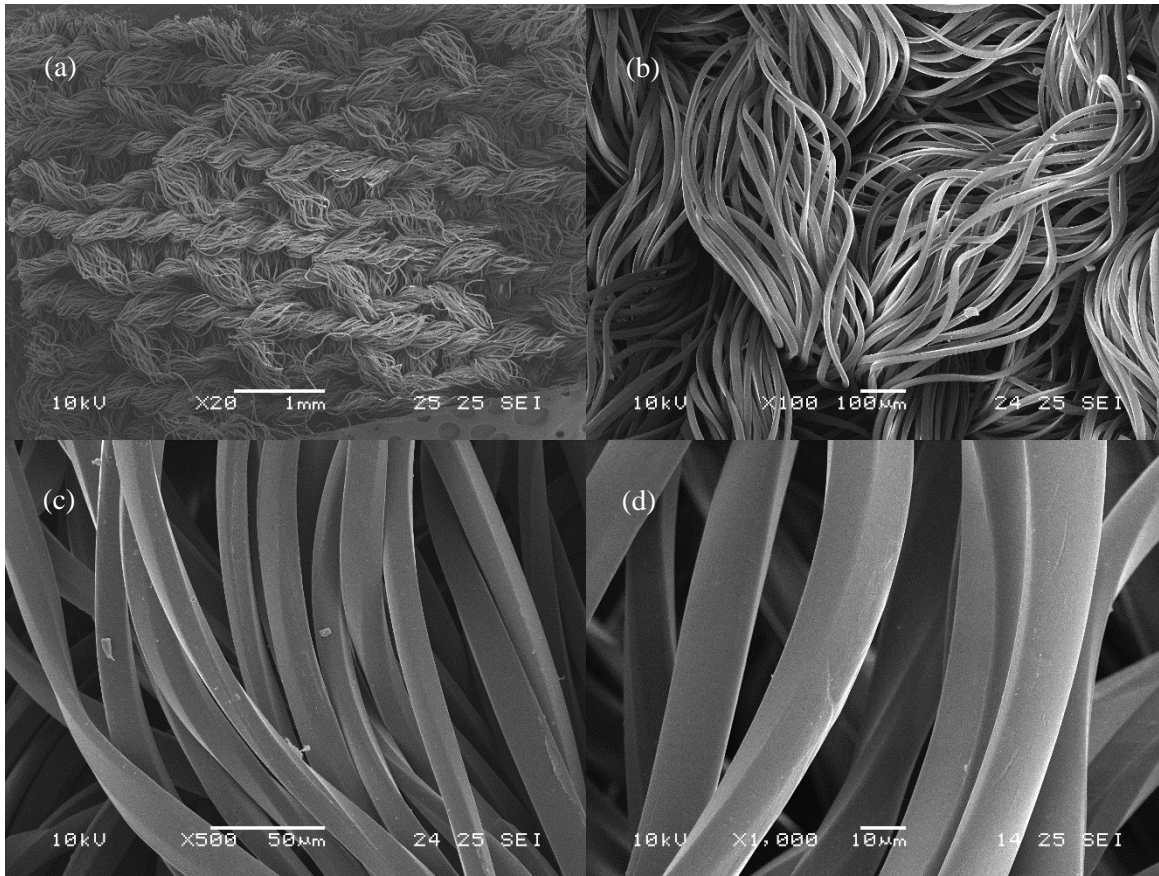


Figure 4.4. SEM images of virgin polyester at (a) x20 (b) x100 (c) x500 and (d) x1000 magnifications.

The cross section of polyester was also imaged, as shown in Figure 4.5. Individual fibres can be seen very clearly but in most cases it is difficult to distinguish the different yarns as the structure is open, although one can be seen in images (b) and (c). It should be noted that some of the fibres may have been flattened during cutting.

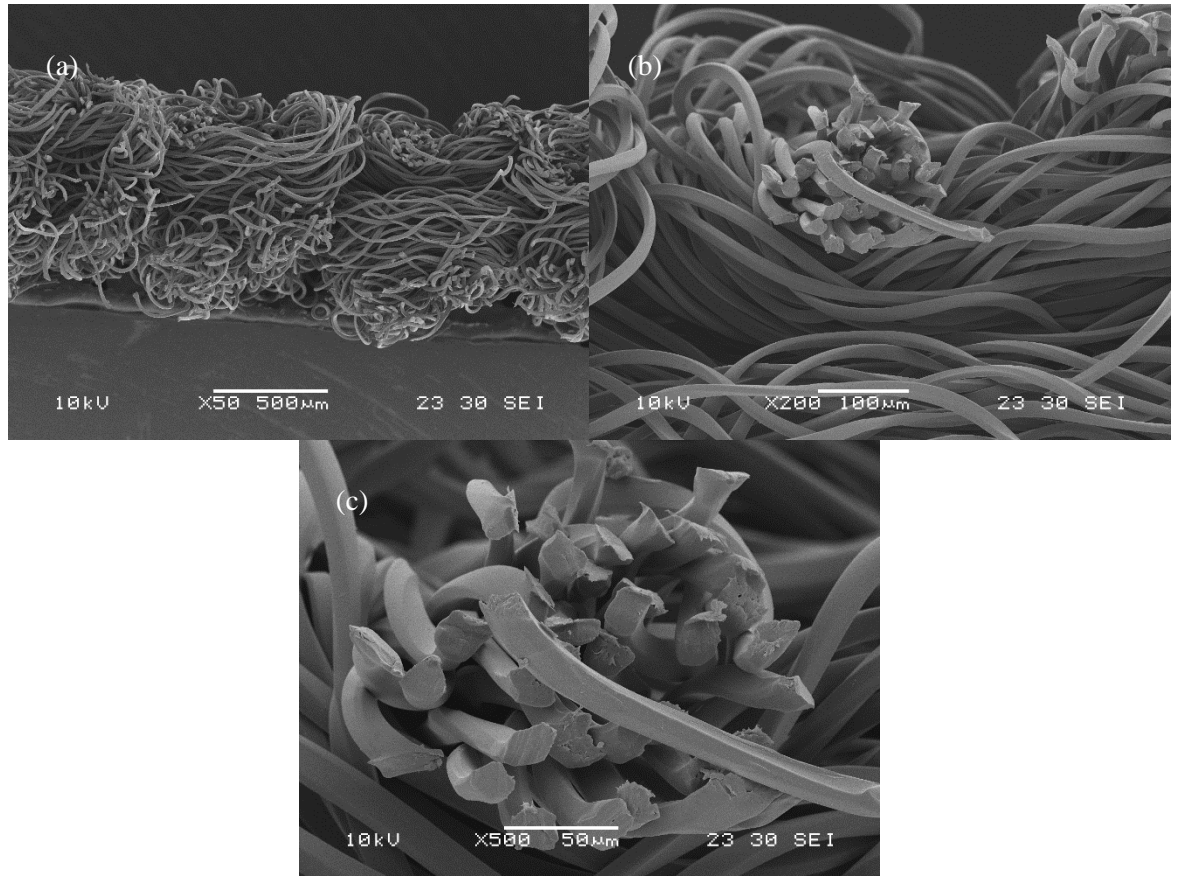


Figure 4.5. SEM images of the cross section of virgin polyester at (a) x50 (b) x200 and (c) x500 magnifications.

4.1.3.2. Cotton

SEM images of cotton (Figure 4.6) at x20 and x100 magnification show the weave pattern is much more regular than polyester, and yarns can be seen to be much more tightly bound. Intra yarn pores are negligible, and inter yarn pores also appear very small. At the higher magnification images it can be seen that the cotton fibres are ribbon like, in that they are flatter than polyester fibres and are twisted. We can also see that they do not have a smooth surface and contain many imperfections, which is characteristic of natural fibres.

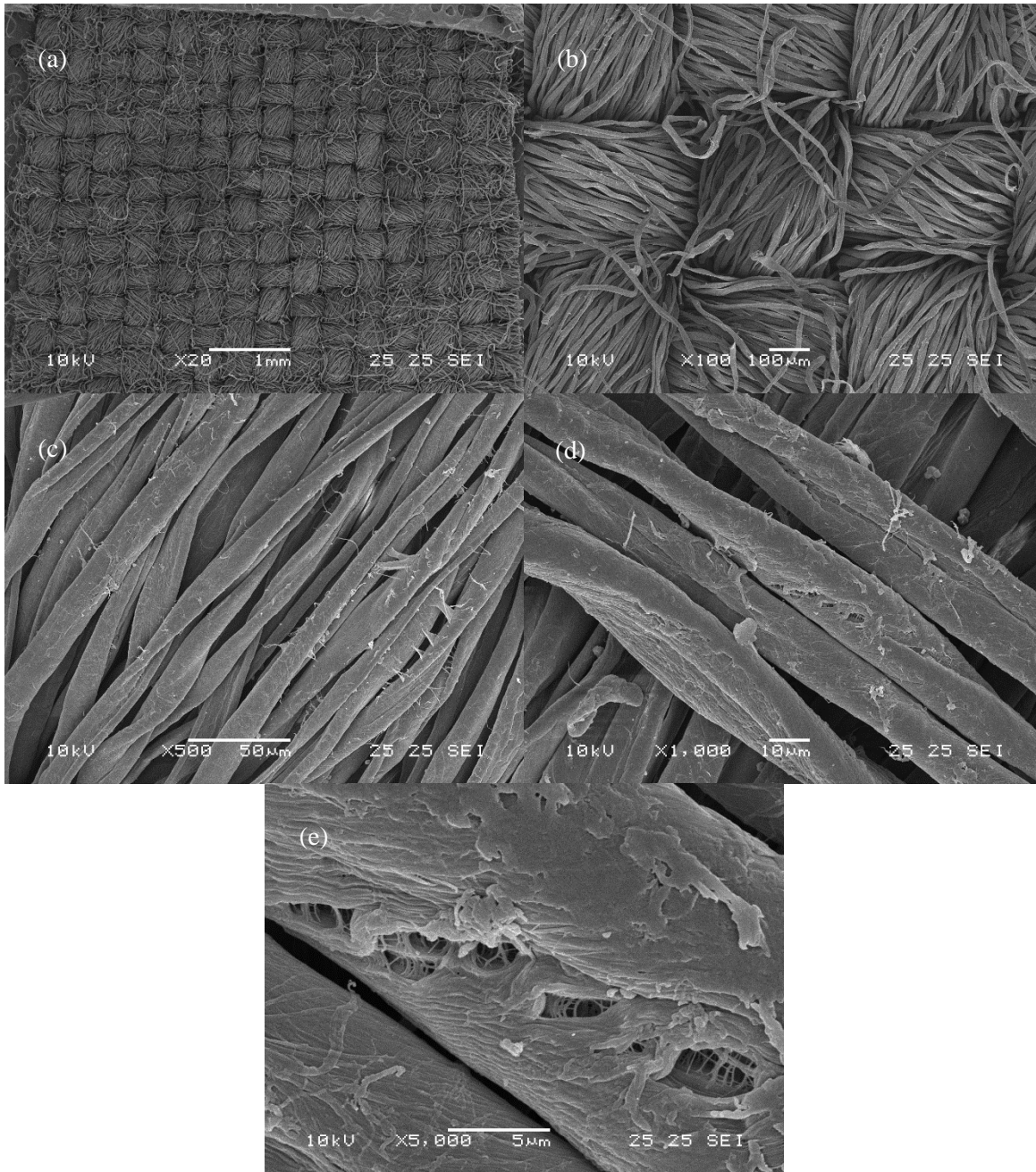


Figure 4.6. SEM images of virgin cotton at (a) x20 (b) x100 (c) x500 (d) x1000 and (e) x5000 magnifications.

SEM images of the cross section of cotton were also acquired (Figure 4.7). Fibres bunched together in yarns can be seen pointing directly towards the front of the image, as well as yarns weaving above and below these. The structure of the fabric appears to be very uniform and yarns are quite dense containing many individual fibres. Again, some of the fibres may have been flattened during cutting.

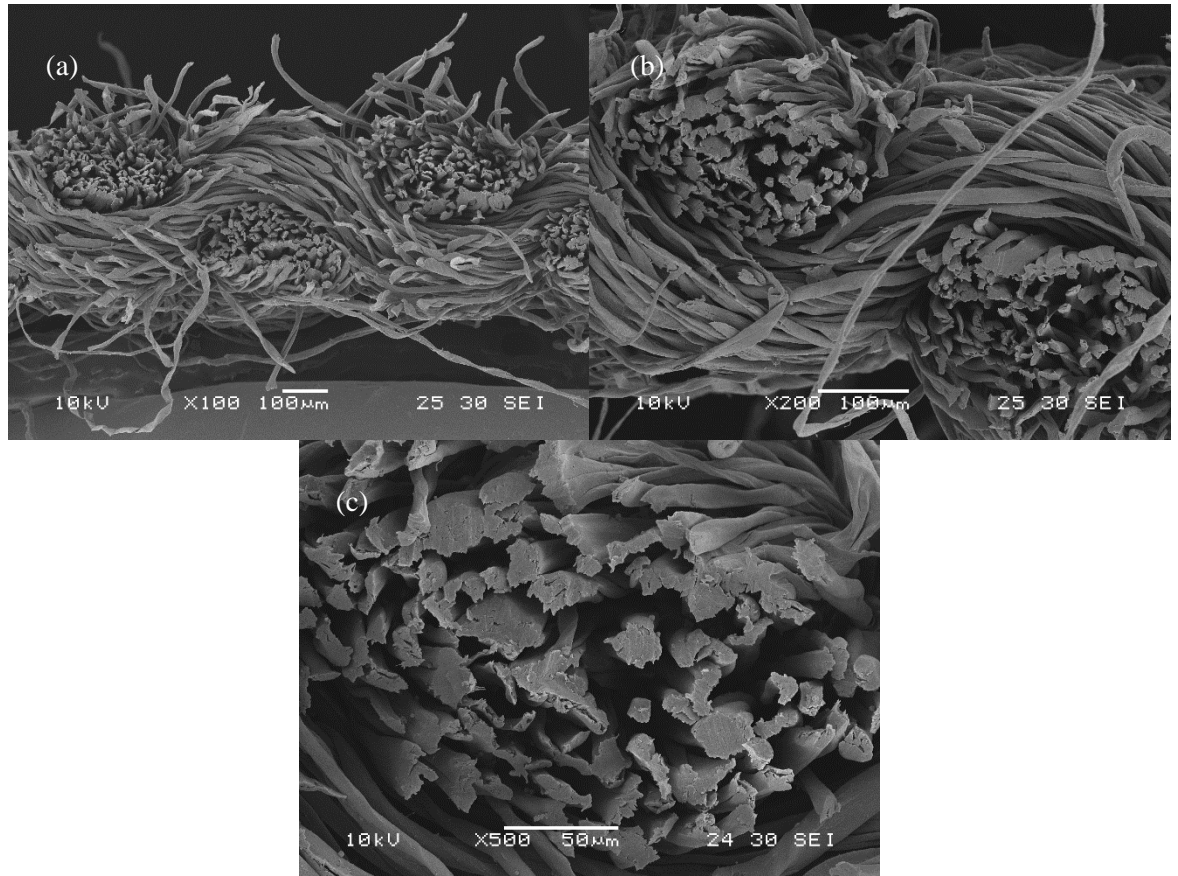


Figure 4.7. SEM images of the cross section of virgin cotton at (a) x100 (b) x200 and (c) x500 magnifications.

4.1.4. Contact Angle

When using the sessile drop method it was found that the water or oil soaked into the fabric immediately; too quickly to allow any analysis. The captive bubble method was used instead and results for cotton, polycotton and polyester are shown in Figure 4.8. It should be noted that when using the captive bubble method a larger contact angle indicated a more hydrophilic fabric surface. Ten bubbles were formed on three separate pieces of fabric. Right and left angle readings were recorded giving a total of 60 angle measurements per fabric. Differences from T-tests are presented in Table 4.3. All fabrics were found to be significantly different.

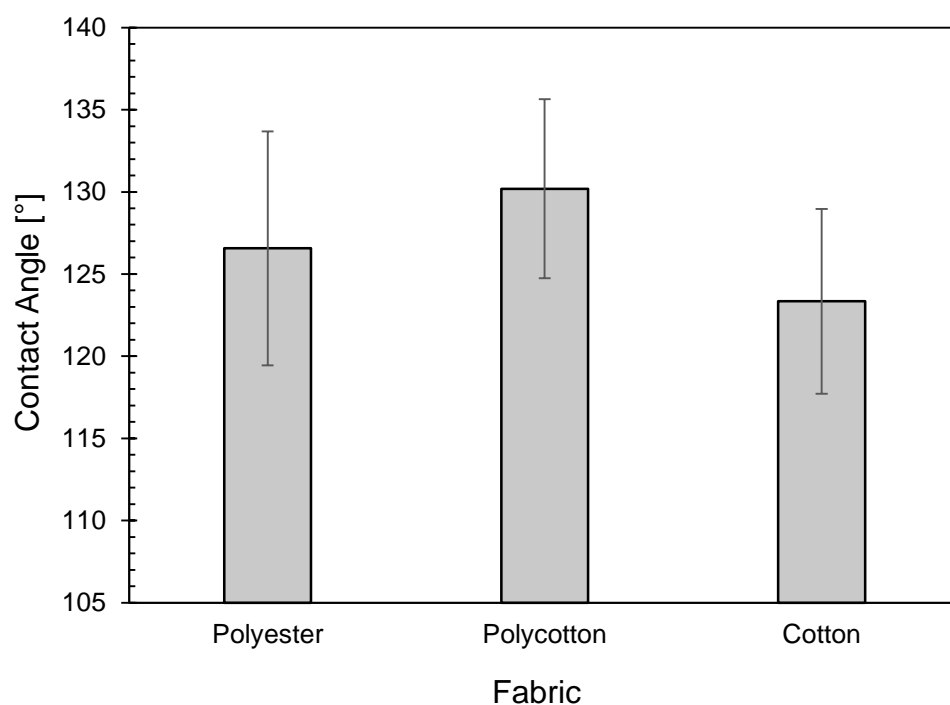


Figure 4.8. Contact angles of polyester, polycotton and cotton found using the captive bubble method.

Table 4.3. Results of t-tests for significant differences between contact angle measurements for polyester, polycotton and cotton using the captive bubble method.

Pair of fabrics	T-test result	Significance
Polyester and Polycotton	6.8×10^{-3}	Fabrics are significantly different
Polyester and Cotton	2.2×10^{-3}	Fabrics are significantly different
Polycotton and Cotton	5.0×10^{-10}	Fabrics are significantly different

The most hydrophilic fabric was found to be polycotton, followed by polyester then cotton. This is surprising as cotton is traditionally thought to be more hydrophilic. This may be due to a coating on the surfaces of the fabrics that has not been removed during prewashing.

4.1.5. Drying time of fabrics

Drying time of fabrics was investigated to develop protocol for analysis prior to experiments, and to gain insight into the relative moisture uptake and drying of the different fabric type, as shown in Figure 4.9. It is concluded that polyester and cotton fabrics should be dried in the fume hood for 3

hours prior to mass, colour and resistance analysis. Polyester fabrics absorbed more water than cotton fabrics, which is as expected when the contact angle results in section 4.1.4 are considered. The rate of drying of both fabrics is very similar.

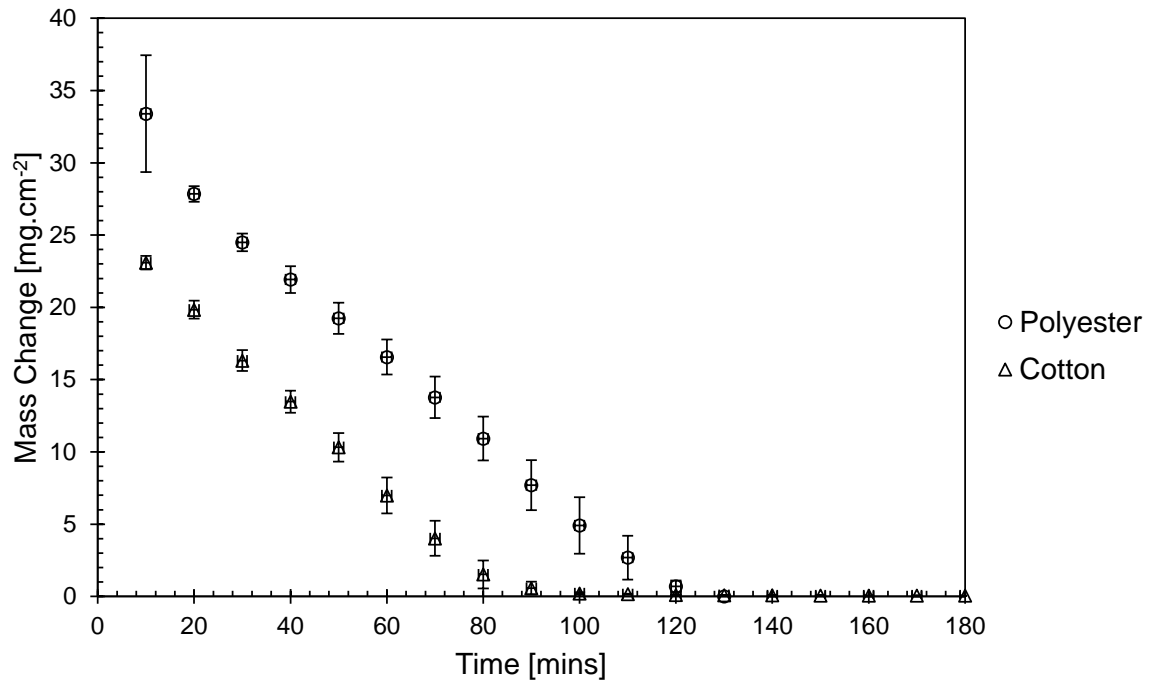


Figure 4.9. Drying time of cotton and polyester fabrics.

4.1.6. Yarn and Fibre Size

Polyester

Ten microscope images of yarns and ten images of fibres, like those shown in Figure 4.10, were used to measure the average diameter of yarns and fibres. For polyester the yarn was found to be $770 \pm 96 \mu\text{m}$ and the fibre was found to be $30 \pm 5.1 \mu\text{m}$.

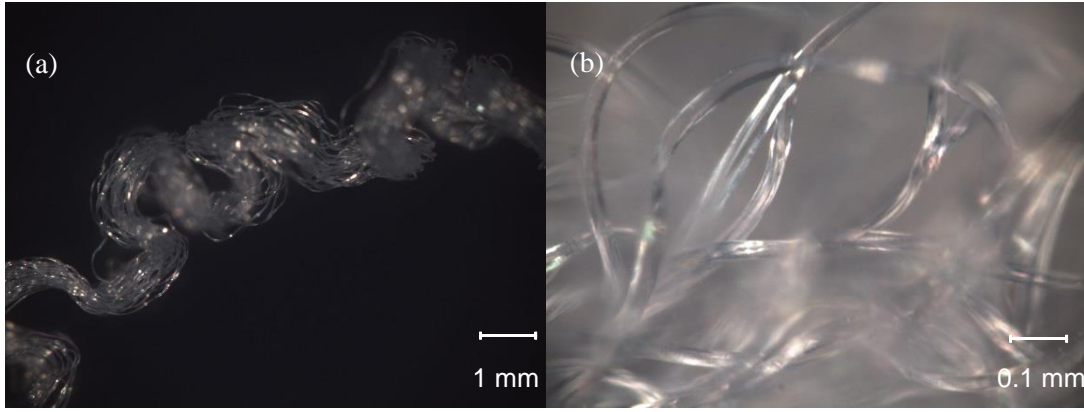


Figure 4.10. Microscope images of virgin polyester (a) yarns and (b) fibres.

Cotton

Imaging was repeated for cotton (Figure 4.11) and the width of the yarn was found to be $520 \pm 77 \mu\text{m}$ and the width of the fibre was found to be $24 \pm 5.7 \mu\text{m}$.

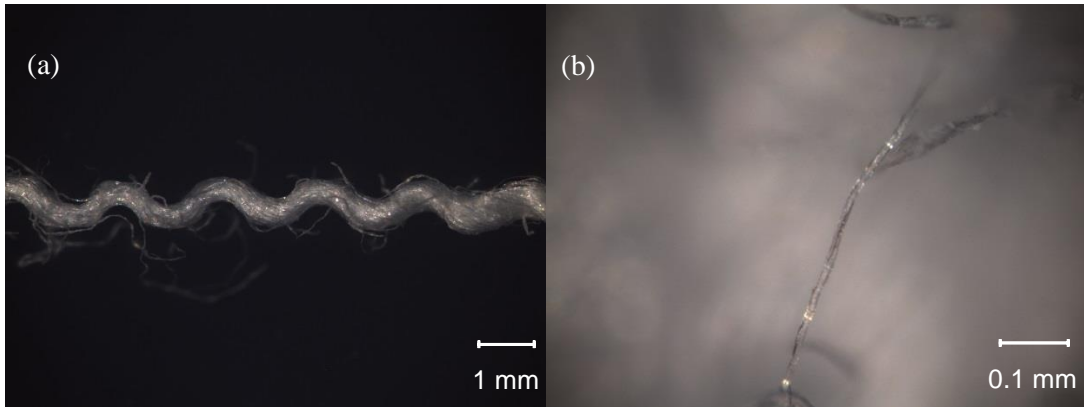


Figure 4.11. Microscope images of virgin cotton (a) yarns and (b) fibres

4.1.7. Pore size

Polyester

Microscope images of polyester are shown in Figure 4.12. MATLAB was used to determine the average pore area after thresholding and closing, which was found to be $12600 \pm 37300 \mu\text{m}^2$. If the pores are assumed to be circular the diameter would be $63 \pm 94 \mu\text{m}$ and if the pores were square the diameter would be $110 \pm 170 \mu\text{m}$.

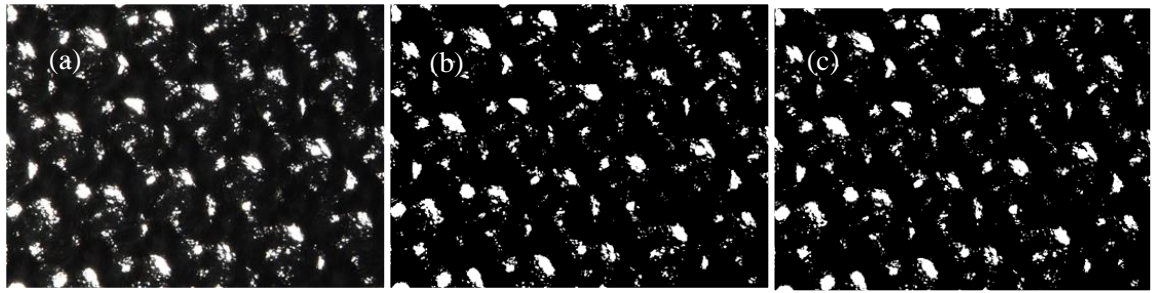


Figure 4.12. Microscope images of polyester used to calculate pore size (a) original image, (b) thresholded image and (c) closed image.

The range of size of pores is very large, causing the standard deviation to be greater than the mean. This is quite evident from the images, as a small number of pores appear very large, and others are very small dots. Figure 4.13 confirms this and shows the pore size distribution.

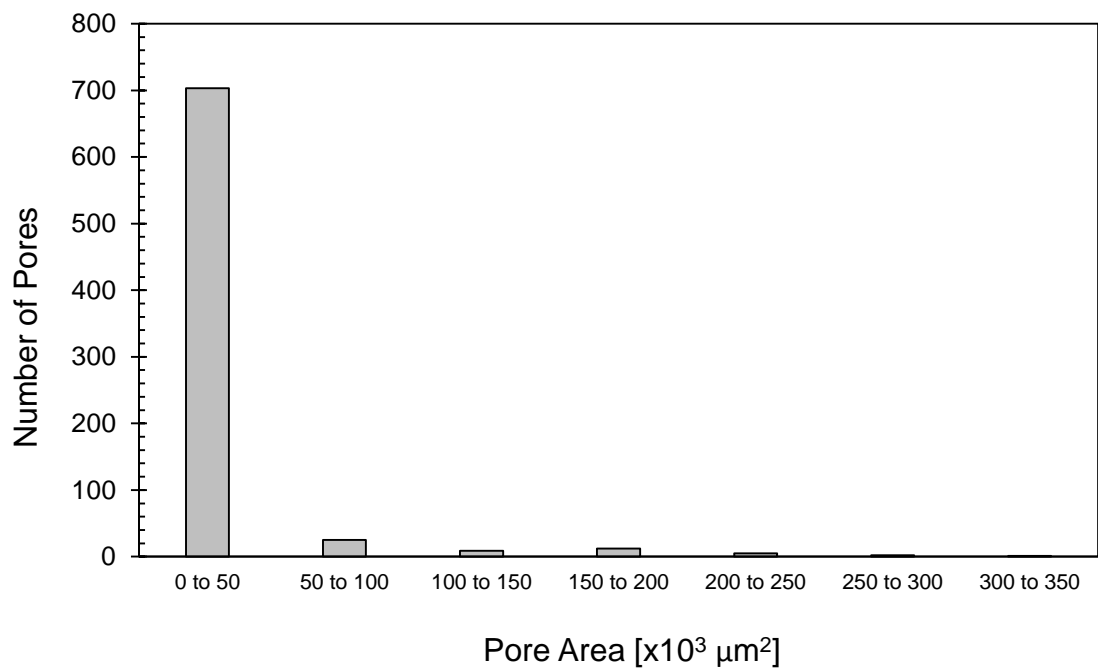


Figure 4.13. Pore size distribution of polyester pores.

When polyester is soiled the topside and underside appear almost equally coloured (Figure 3.3). During soiling, when sebum is applied to the fabric, some of the sebum will move through the larger pores, allowing soiling of both sides.

Cotton

Figure 4.14 shows microscope images of cotton fabric. The average pore area was found to be $39400 \pm 22500 \mu\text{m}^2$. If the pores are assumed to be circular the diameter would be $112 \pm 32.0 \mu\text{m}$ and if the pores were square the diameter would be $199 \pm 56.7 \mu\text{m}$.

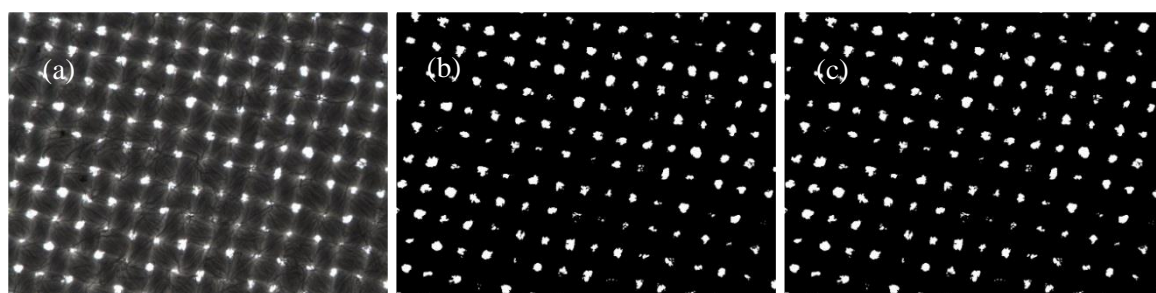


Figure 4.14. Microscope images of cotton used to calculate pore size (a) original image, (b) thresholded image and (c) closed image.

Figure 4.15 shows the pore size distribution of the cotton pores. It is clear from this graph and from the images above that the pore size in cotton fabrics is much more consistent than polyester, but that there is still some variability.

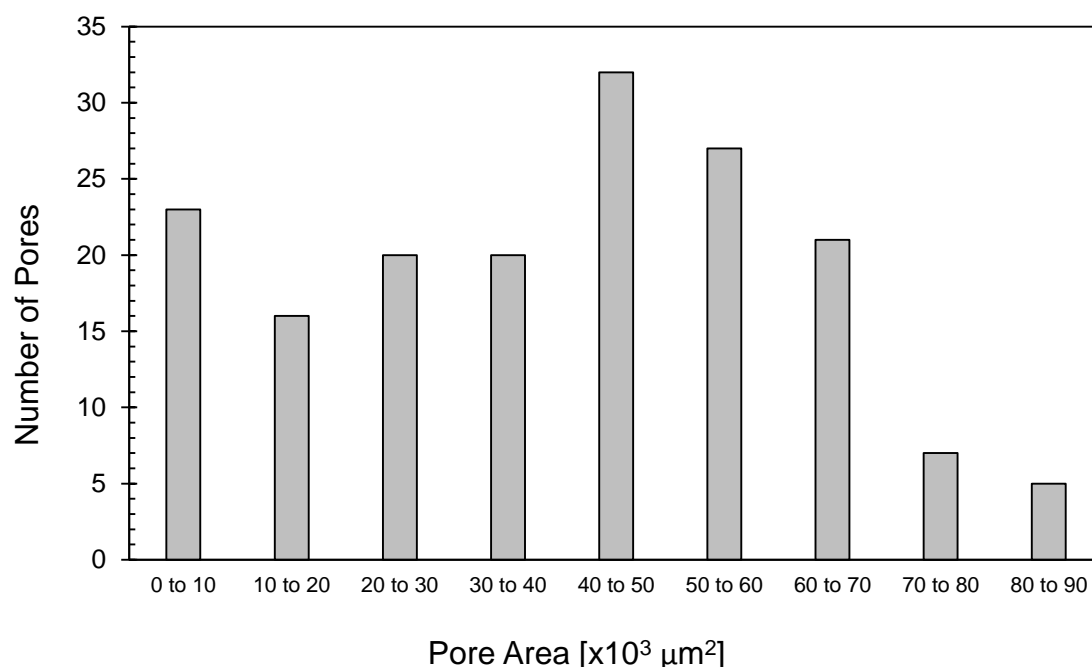


Figure 4.15. Pore size distribution of cotton pores.

Unlike polyester, the topside and underside of the soiled cotton are distinguishable (Figure 3.4). The sebum does not move through the pores of the fabric to the same extent as it does with polyester as the pores are much smaller.

4.2. Soil

4.2.1. FTIR

4.2.1.1. Sebum

Figure 4.16 shows the FTIR spectrum of sebum. Sebum contains a mixture of saturated and unsaturated carboxylic acids, triglycerides, alcohols and other hydrocarbons. Although identification of individual components is not possible, using FTIR a characteristic spectrum of sebum was found, which was compared with soiled and cleaned fabrics later in this thesis.

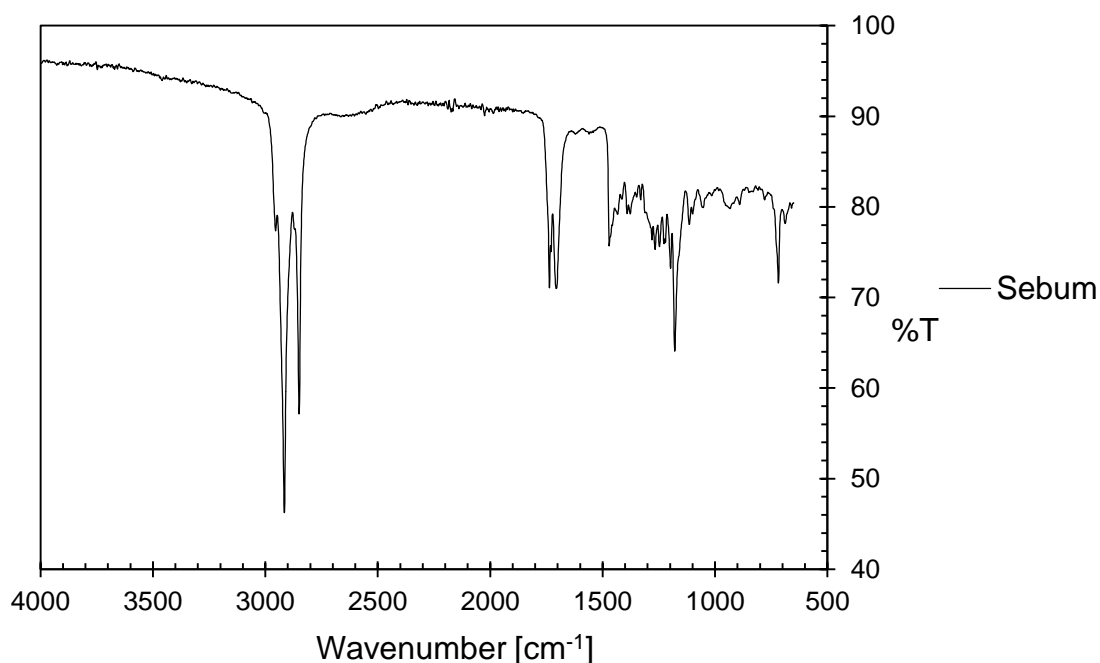


Figure 4.16. FTIR spectrum of sebum.

Table 4.4. Peak table for FTIR of sebum.

Peak (cm ⁻¹)	%T	Assignment
2954	77.36	=C-H stretch
2916	46.24	C-H stretch
2849	57.17	C-H stretch
1736	71.08	C=O stretch
1706	70.98	C=O stretch
1471	75.68	CH ₂ bend
1391	79.27	O-H bend
1376	79.3	O-H bend
1179	64.06	C-O stretch
718	71.58	C-H bend

4.2.1.2. Soiled polyester

Soiled polyester samples show very little difference between the top and under surfaces, as shown in Figure 3.2, and contains a thick layer of sebum. This is confirmed by the FTIR spectra of the top and under surfaces, which are compared to sebum and virgin polyester in Figure 4.17. The sebum peaks including the characteristic peaks at just under 3000 cm⁻¹ are visible on both top and under soiled surfaces. The polyester peaks, for example at 1242 and 1095 cm⁻¹, are completely masked on both the top and under soiled surfaces.

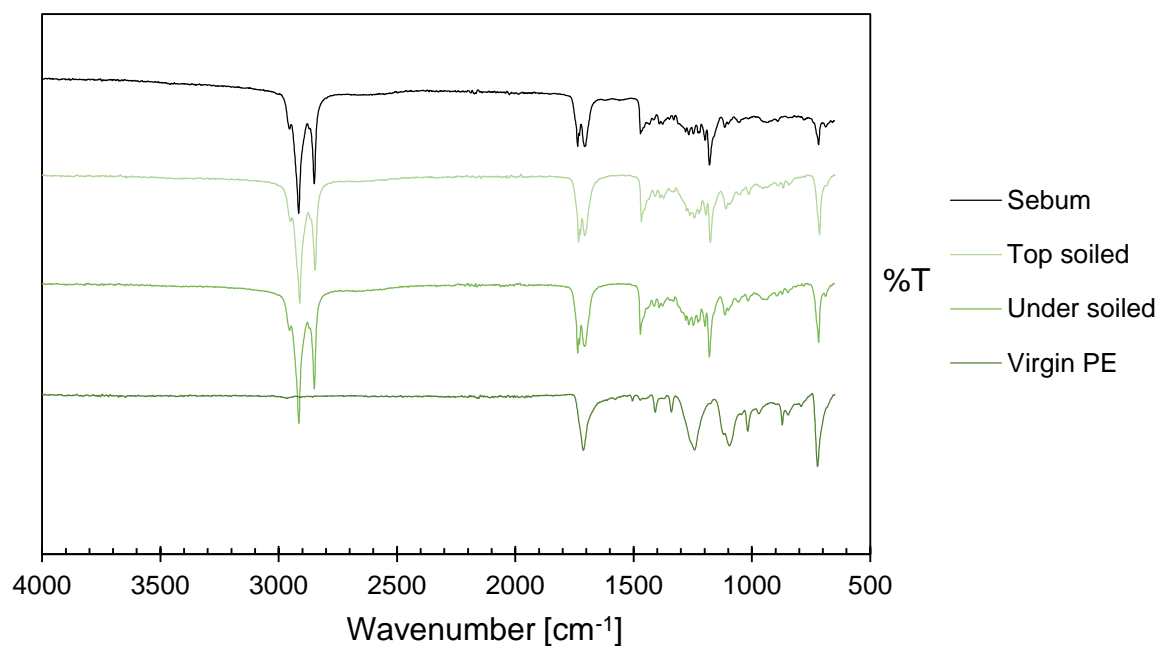


Figure 4.17. FTIR of virgin polyester, soiled polyester and sebum.

4.2.1.3. Soiled cotton

On cotton the soil clearly sits on the surface it has been applied to, with only a small amount of sebum permeating the fabric, as shown in Figure 3.3. Cotton samples have less sebum on the surface than polyester. Figure 4.18 shows an FTIR spectra of the sebum, top surface and under surface of the soiled cotton fabric, and virgin cotton. It can be seen that the top soiled surface contains all of the distinctive sebum peaks identified in 4.2.1.1, and the characteristic broad O-H peak from cotton at 3339 cm^{-1} and collection of peaks at just above 1000 cm^{-1} are somewhat masked. In line with visual observations, the under soiled fabric surface contains more dominant cotton peaks, whereas the sebum peaks have reduced in size.

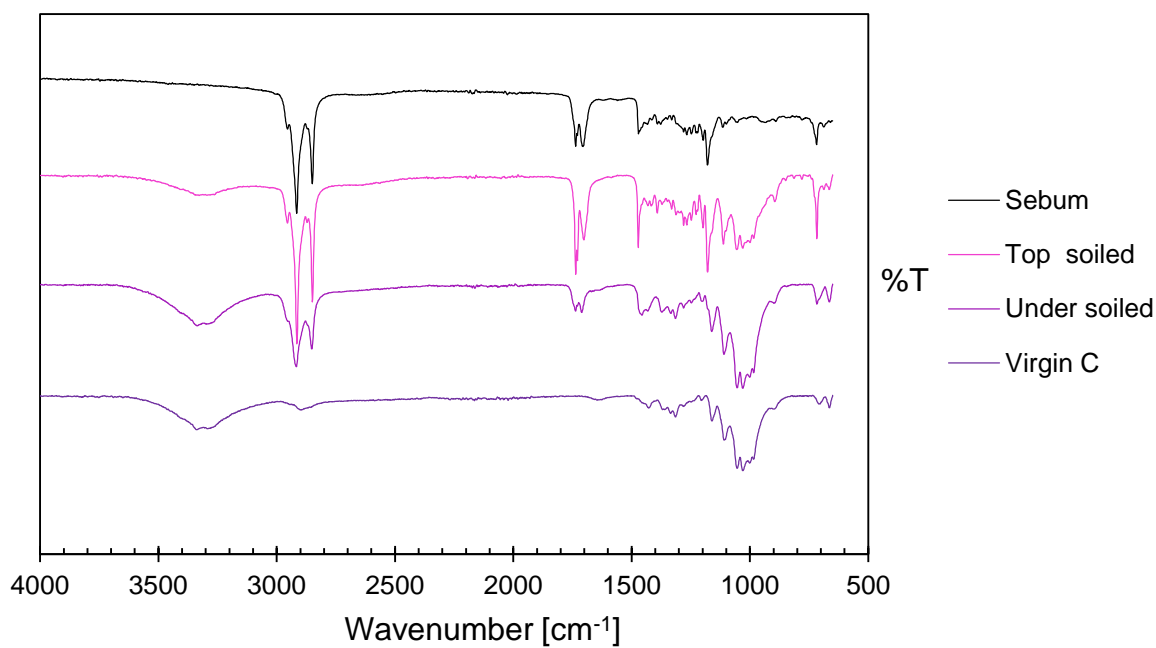


Figure 4.18. FTIR of virgin cotton, soiled cotton and sebum.

4.2.2. Zeta potential

The zeta potential of virgin and soiled fabric is presented in Figure 4.19. Once again, none of the fabrics tested reach their isoelectric point over the pH range tested. It can be seen that sebum reduces the negative surface charge on both fabrics.

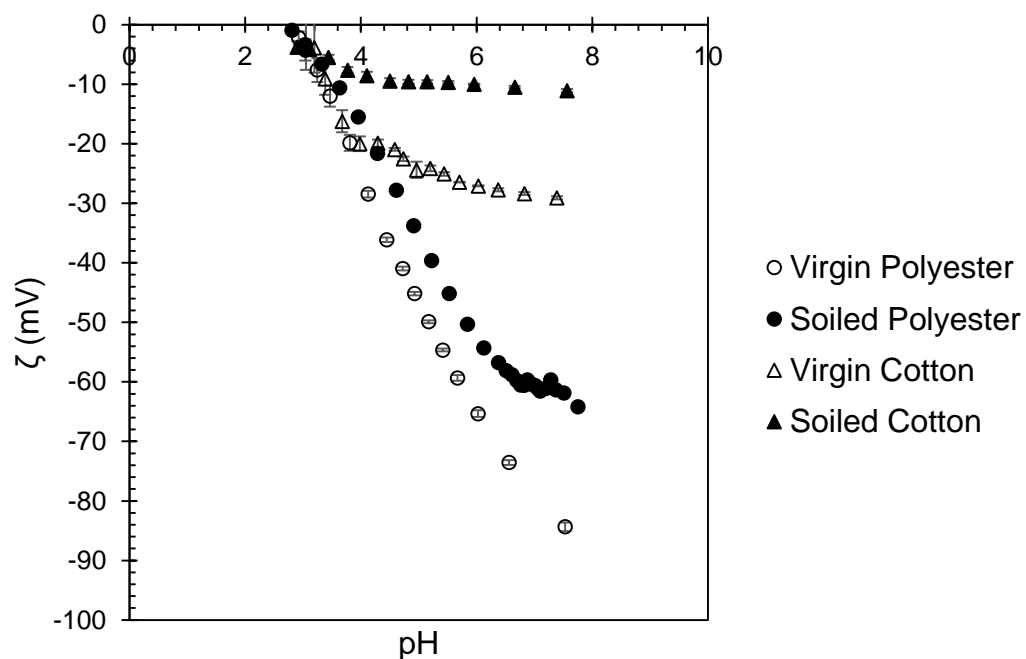


Figure 4.19. Zeta potential of virgin and soiled polyester and cotton. The error bars represent \pm one standard deviation for four repeat measurements taken on each fabric.

4.2.3. SEM

4.2.3.1. Sebum

SEM images of sebum were acquired to investigate its appearance. The images below, Figure 4.20, show that the sebum does not form a uniform surface. Some areas of the sebum are smooth, others are globular and some appear grainy.

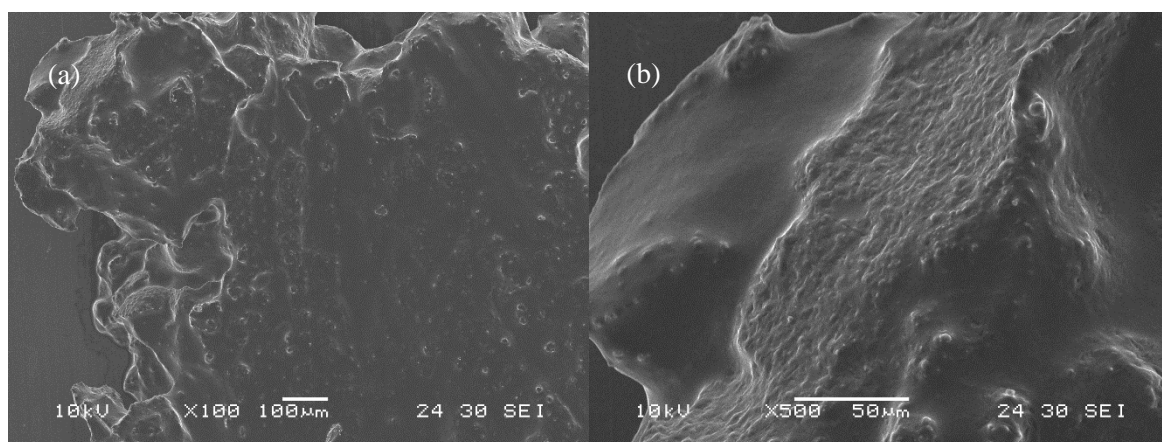


Figure 4.20. SEM images of sebum at (a) x100, and (b) x500 magnifications.

4.2.3.2. Polyester

SEM images of soiled polyester, Figure 4.21, show the sebum sits within the yarns filling both inter yarn and intra yarn pores, and bridges between adjacent fibres. Some of the pores are not fully covered with sebum, which may be due to the large pore size. Image (d) has focused on a fibre, and deposits of sebum can clearly be seen on the surface. Unlike cotton, polyester fibres have a smooth surface with very few imperfections therefore these imperfections cannot come from the fibre itself. Image (e) has focused on an area between two fibres and shows clearly that the sebum is globular.

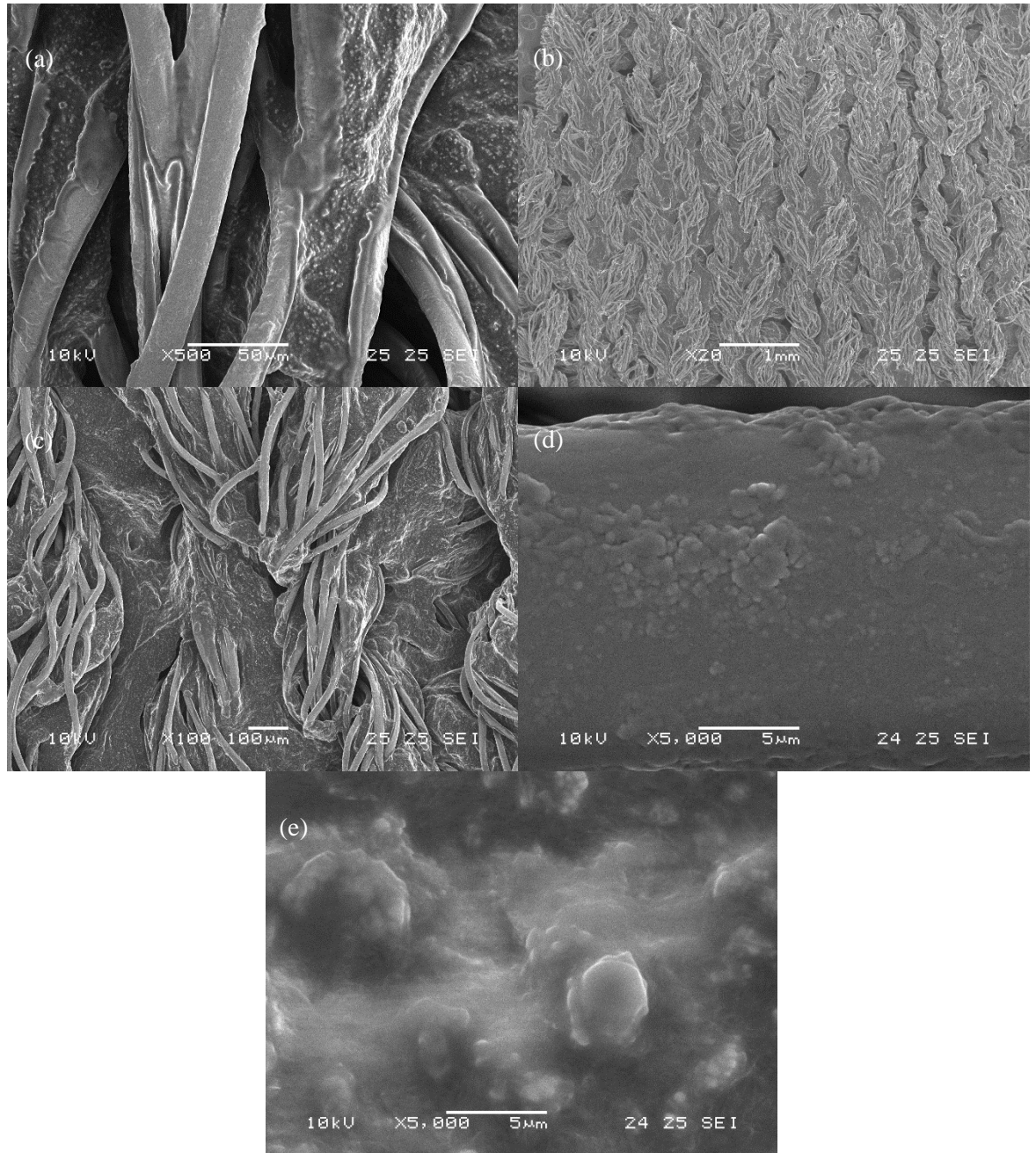


Figure 4.21. SEM images of polyester soiled with sebum at (a) x20, (b) x100, (c) x500 and (d, e) x5000 magnifications.

Cross sectional SEM images of soiled polyester were also taken, as shown in Figure 4.22. It can be seen that large amounts of sebum sit in between yarns but much less sebum can be seen within these yarns pointing directly towards the SEM. This means the sebum is sitting in the large inter yarn pores. Also, more sebum can be seen sitting on the surface of the fabric, with some sebum clearly moving

through the fabric to occupy gaps between yarns. The grainy, uneven texture of sebum can again be seen.

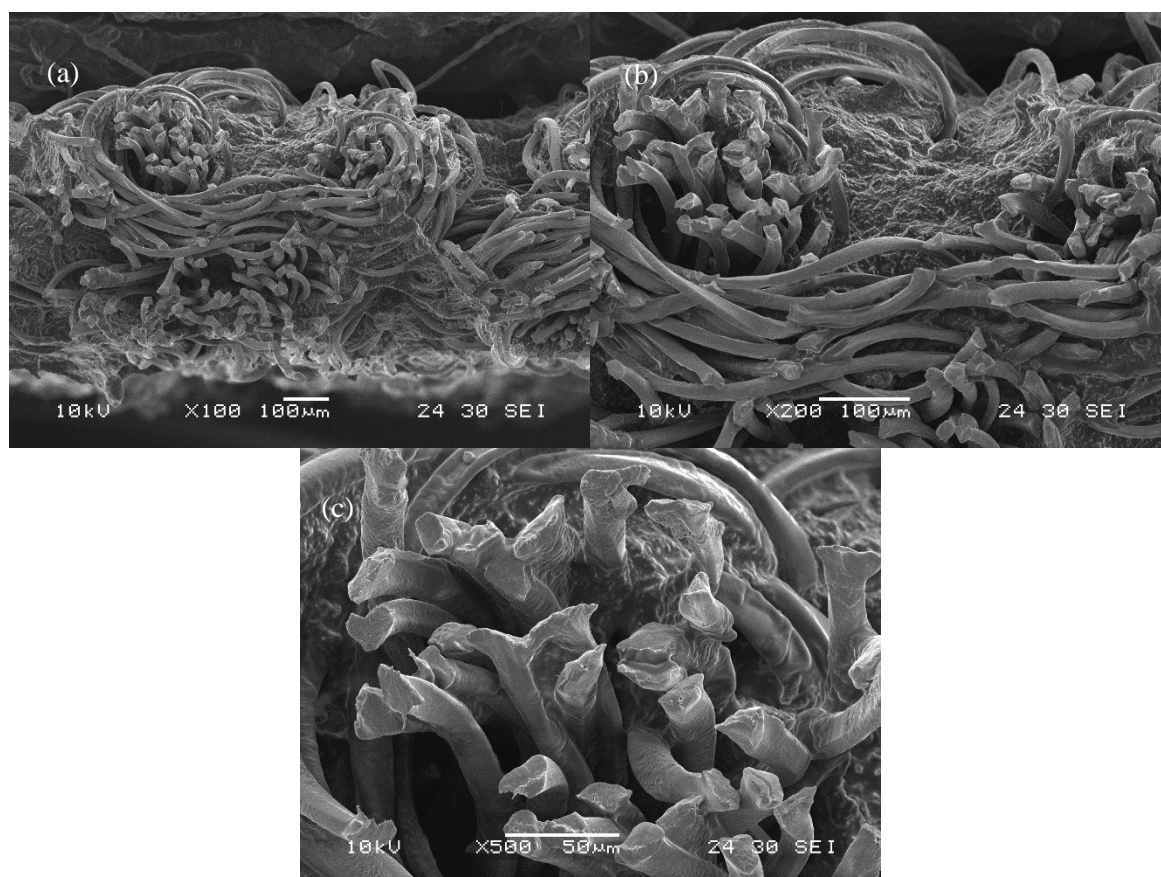


Figure 4.22. SEM images of the cross section of polyester soiled with sebum at (a) x100, (b) x200 and (c) x500 magnifications.

4.2.3.3. Cotton

SEM images of cotton soiled with sebum, Figure 4.23, don't show any obvious differences between the soiled sample and virgin cotton (Figure 4.6) at x20 and x100 magnifications. At x500 and x1000 it is more difficult to tell on the fibre itself what are imperfections in the cotton and where sebum has been deposited, however sebum bridging between adjacent fibres is quite obvious. Images at x5000 of the sebum coated fibre and of sebum between two fibres show the same globular structure as the polyester images. Image (e) shows the sebum sitting within the ribbon like structure of the fibre, and it is likely the sebum may be covering imperfections on the fibre and some sebum may sit within the

fibre itself, something which is not possible with polyester as it is a synthetic fibre and does not contain intra fibre pores.

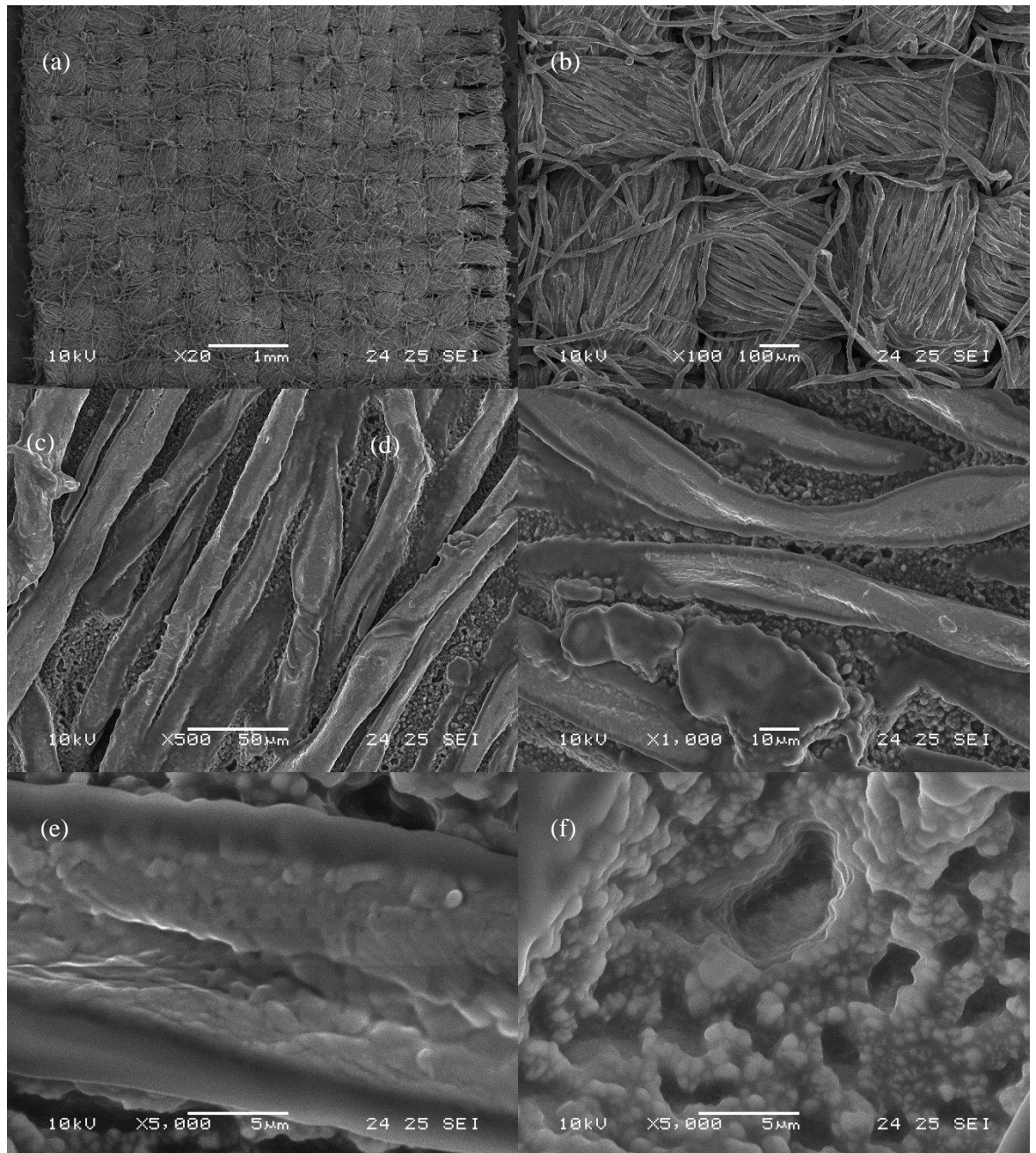


Figure 4.23. SEM images of cotton soiled with sebum at (a) x20, (b) x100, (c) x500 and (d) x1000 and (e, f) x5000 magnifications.

SEM images of the cross section of cotton soiled with sebum have also been acquired, as shown in Figure 4.24. It can be seen that much of the sebum sits on the top surface, the side it has been applied to, and the fibres within the yarns pointing towards the SEM are only coated if they are near to this

surface. Penetration of the fabric by the sebum is significantly less than for polyester. Sebum appears to sit across the top of the surface, blocking the inter yarn pores. This is possible as the pores are much smaller for cotton than polyester.

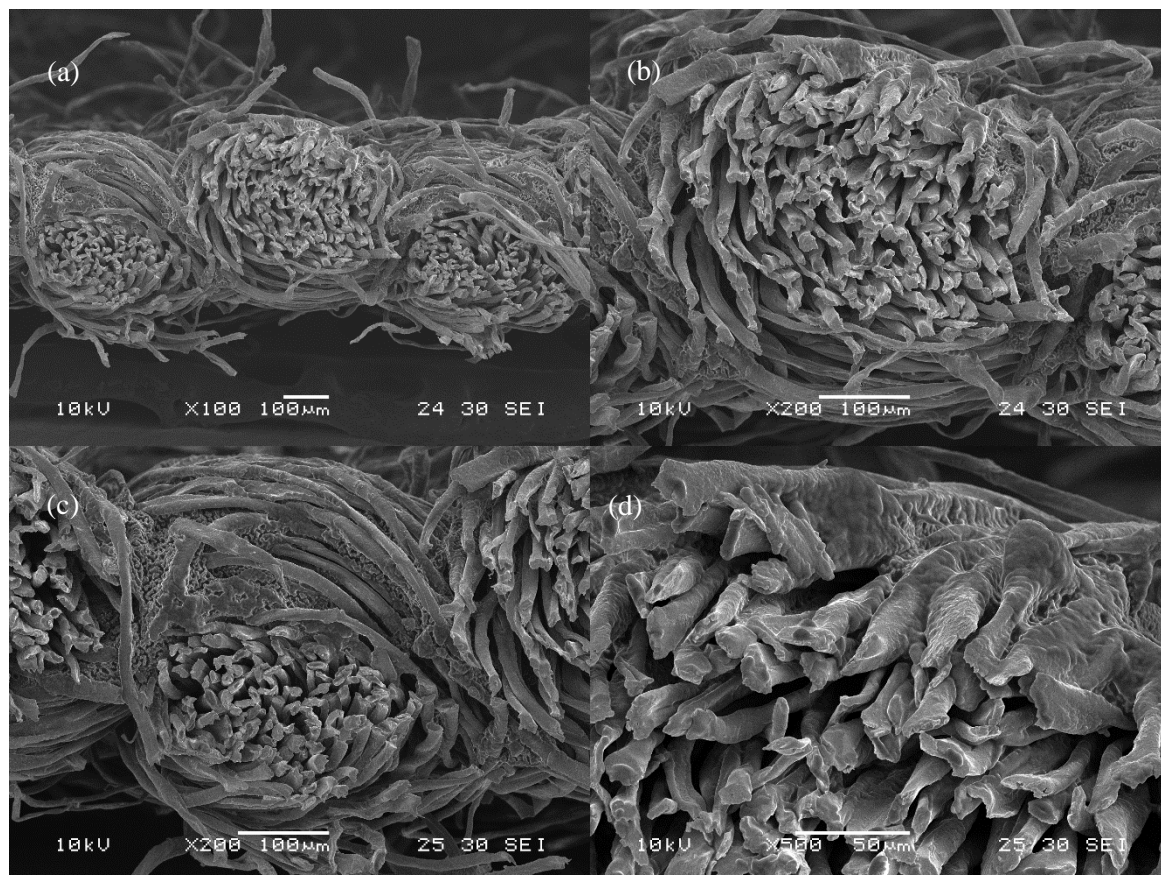


Figure 4.24. SEM images of the cross section of cotton soiled with sebum at (a) x100, (b, c) x200 and (d) x500 magnifications.

4.2.4. Differential scanning calorimetry

Differential scanning calorimetry (DSC) was carried out by Dr Ian Tucker at Unilever, Port Sunlight. The first heating ramp, shown in Figure 4.25(a), shows a graph with two distinct regions, indicating that the sebum contains different phases with different melting behaviours. A fraction of the mixture becomes liquid at 20.3 °C, whereas much of the mixture is not liquid until 35.7 °C is reached. At 70 °C all constituents have melted and the solution forms a homogeneous mixture. When this is then cooled and the process repeated we no longer see two distinct regions, and instead see one large region. This is likely to be because the mixture has been cooled rapidly and as such has not separated

into different fractions, instead forming a more homogenous mixture. Both graphs seem to suggest that all constituents of sebum have melted by about 40 °C, although this is not a simple process due to the complex make-up of the sebum.

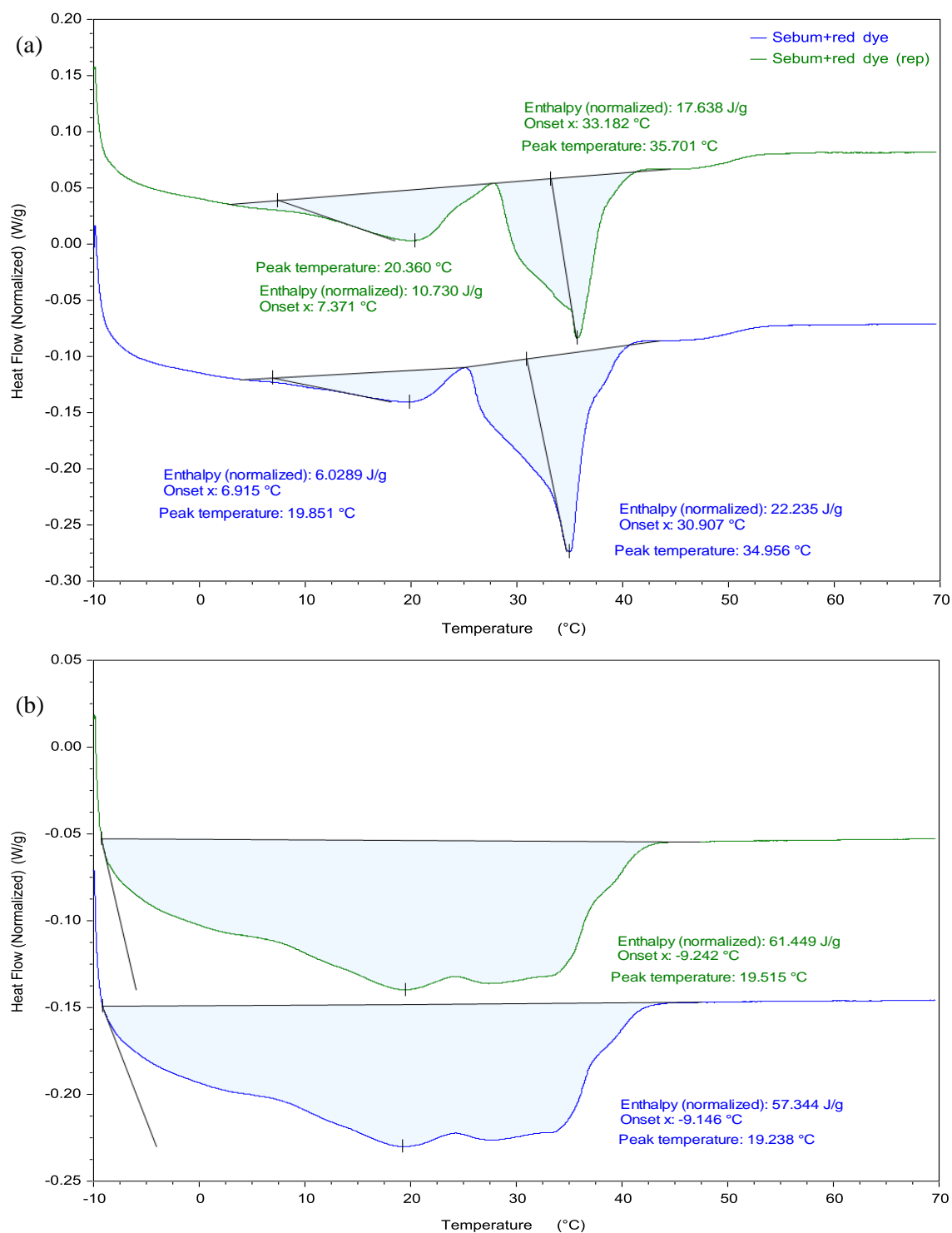


Figure 4.25. DCS of sebum, (a) shows the first heating ramp after sebum is cooled from room temperature and (b) shows the second heating ramp when sebum has cooled from 70 °C

4.3. Consistency of soiled fabric samples

Fabrics supplied by Equest were tested for consistency using the three methods planned for analysis of fabrics before and after cleaning – mass, colour and resistance.

4.3.1. Consistency of Mass

Both lengths of fabric were weighted for cotton and polyester, 10 fabrics of each length therefore 20 samples of each fabric. The average mass per unit area was found for each sample and is presented in Table 4.5. Fabrics with sebum were then weighed, and the mass per unit area of sebum was also calculated. It can be seen that cotton has a higher mass per unit area than polyester, but polyester samples contain significantly more sebum than cotton. This is in line with the images found in Figure 3.3 and 3.4.

Table 4.5. Mass per unit area of polyester and cotton, and sebum added to these fabrics.

	Mass of fabric per unit area (mg.cm ⁻²)	Mass of sebum per unit area (mg.cm ⁻²)
Polyester	12.12 ± 0.21	32.30 ± 1.61
Cotton	16.87 ± 0.70	9.687 ± 0.49

It was also important to test whether storage conditions prior to mass measurements significantly altered results. Initially, fabrics were stored in the fridge and the mass measured immediately upon removal. Fabrics were then stored in the fume hood for a minimum of three hours then reweighed. Table 4.6 shows results of t-tests performed between fabrics measured from the fridge and fabrics stored in the fume hood. For all conditions the t-tests show there is no significant difference.

Table 4.6. Results of t-tests between fabrics stored in the fridge or fume hood prior to mass measurement

Condition	t-test value	Result
35.5 cm Polyester Blank	0.9518	No significant difference
56 cm Polyester Blank	0.8364	No significant difference
35.5 cm Polyester Stained	0.6778	No significant difference
56 cm Polyester Stained	0.5394	No significant difference
35.5 cm Cotton Blank	0.9199	No significant difference
56 cm Cotton Blank	0.9727	No significant difference
35.5 cm Cotton Stained	0.1205	No significant difference
56 cm Cotton Stained	0.2662	No significant difference

The mass of different areas of soiled samples was also measured. Nine strips of fabric along the length of the fabric were weighed to give a profile of the mass per unit area against distance from the centre of the fabric, as shown in Figure 4.26. The three centre points were taken from the sebum strip on the fabric, and the remaining points were taken from the surrounding unsoiled area. Results confirm earlier findings that unsoiled polyester has a lower mass per unit area than cotton, but a higher mass per unit area of sebum. The mass per unit area of both samples significantly increases in the soiled area.

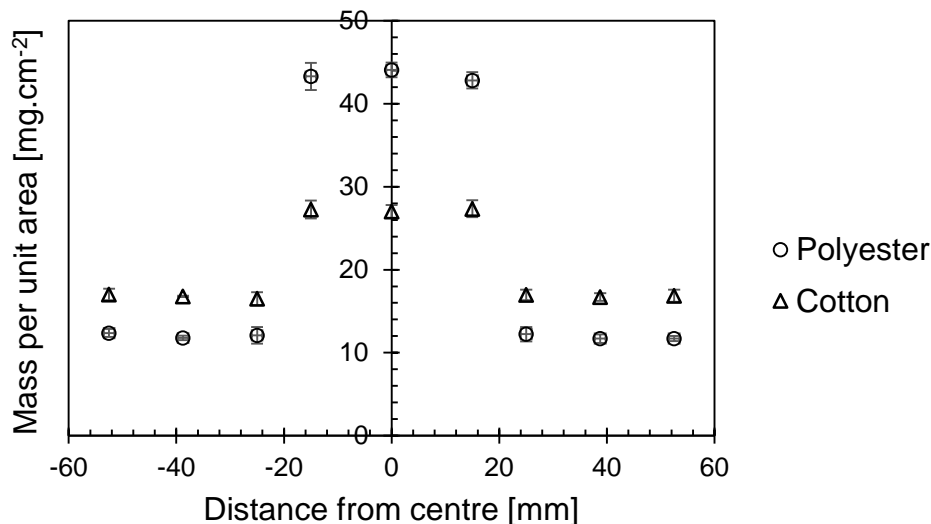


Figure 4.26. Mass per unit area of soiled polyester and soiled cotton.

4.3.2. Consistency of Colour

Fabrics were stored in the fridge prior to measurement using the Spectrophotometer. The colour of blank fabric was measured, as well as both the front and back of the stain strip on stained fabrics. Figure 4.27 (a), (b) and (c) below show results for ΔL^* , Δa^* and Δb^* respectively. All graphs are shown with the same scale. It can be seen that samples do not vary significantly, and unstained fabrics are very different to stained ones. It can also be seen that the front and back of polyester fabrics are very similar. T-tests show no significant difference at the 0.05 level in L value ($t=0.091$), but do show significant differences for a^* and b^* (1.87×10^{-4} and 4.51×10^{-4} respectively). There are much bigger differences between the front and back of the cotton fabrics. This is consistent with what is observed when looking at the fabrics, as shown in Figures 4.2 and 4.3.

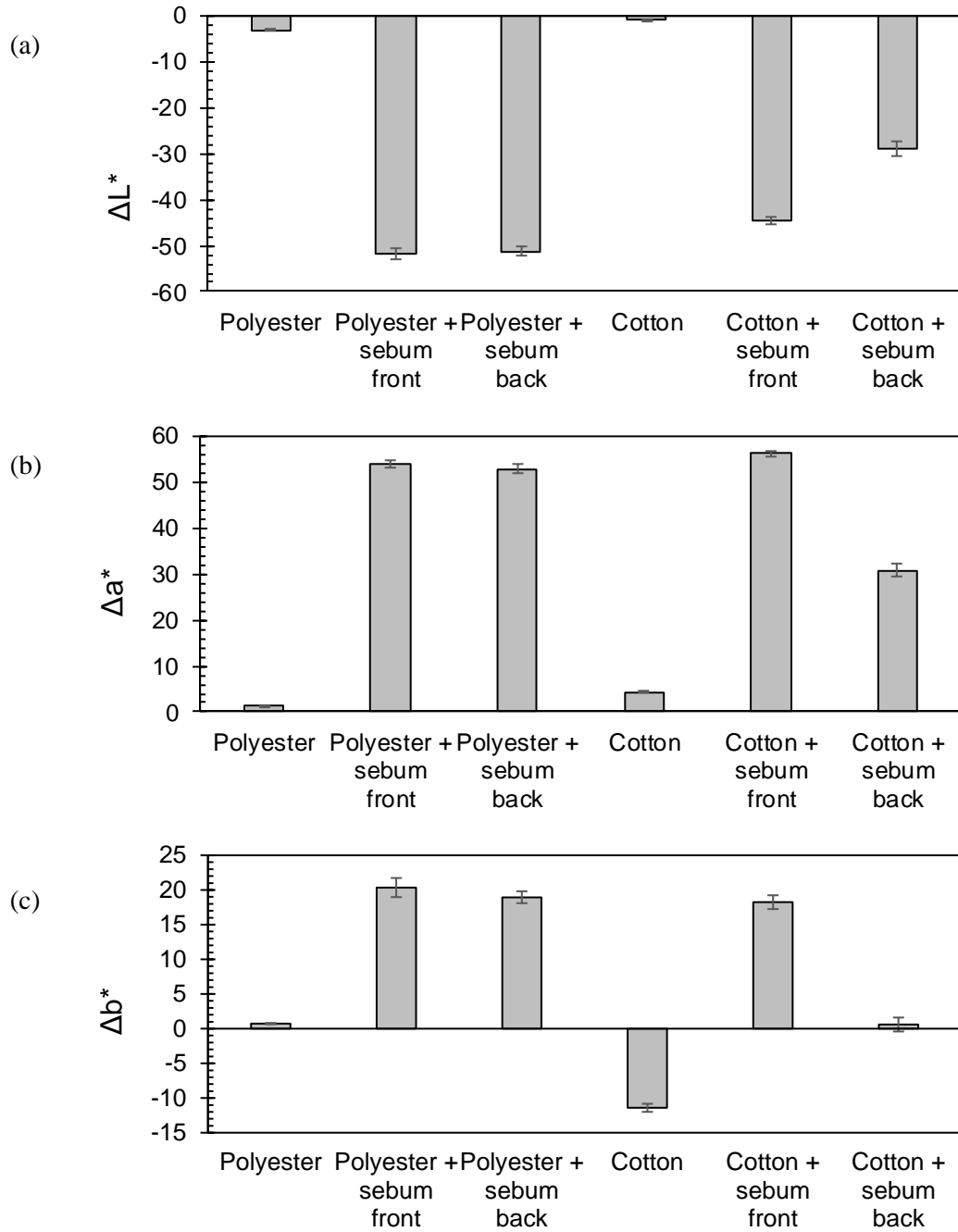


Figure 4.27. Consistency of fabrics results for (a) ΔL^* , (b) Δa^* and (c) Δb^* measures of colour.

4.3.3. Consistency of Resistance to Flow of Water

Table 4.6 shows the resistance of virgin and soiled polyester and cotton fabrics to flow of water. It can be seen that the soiled cotton is 3 orders of magnitude greater than the other samples, which indicates that the sebum has blocked many of the pores of the cotton. Virgin and soiled polyester are

much more similar, which suggests that the sebum does not fully block the pores on this sample. All fabrics show small variability, therefore the method of soiling used is good for producing consistent samples.

Table 4.7. Resistance of virgin and soiled polyester and cotton.

	Resistance of virgin fabric (m^{-1})	Resistance of soiled fabric (m^{-1})
Polyester	$(2.04 \pm 0.13) \times 10^6$	$(5.98 \pm 0.18) \times 10^7$
Cotton	$(1.02 \pm 0.05) \times 10^8$	$(1.63 \pm 0.06) \times 10^{11}$

4.4. Surfactant

4.4.1. CMC of Surfactant

The CMC of LAS is 0.0016 M (Tucker, 2014), however it was important to verify this experimentally. Figure 4.28 shows the interfacial tensions of the LAS solution at a number of concentrations.

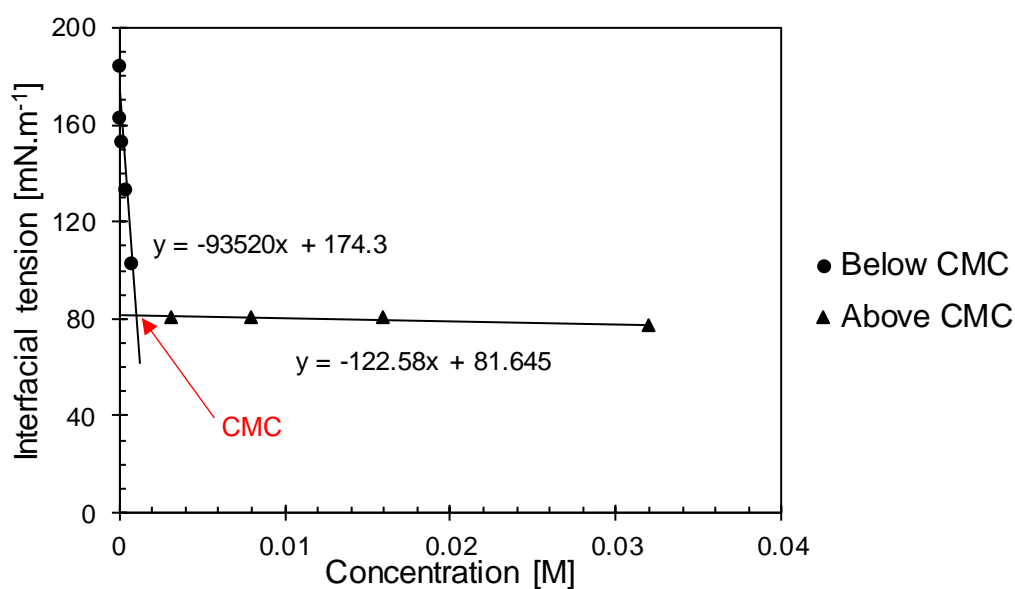


Figure 4.28. Interfacial tension of LAS solution.

Using the graph the CMC was found to be no higher than 0.002 M, therefore the value provided by Tucker was assumed to be correct.

It was of interest to discover whether the concentration of surfactant in experiments performed above the CMC remained above this level after the experiment. For this reason a sample of wash solution from the harshest removal conditions – polyester rubbed at 60 °C with 2 x CMC LAS – was also analysed. The interfacial tension was found to be $46.17 \pm 1.421 \text{ mN.m}^{-1}$. This is significantly lower than results found previously for surfactant in water. It is thought that this may be due to the presence of sebum, which would also effect the interfacial tension.

Chapter 5: Effect of Chemical Action

To investigate the effect of chemical action alone fabrics were soaked in water or surfactant solution at various temperatures. Results are presented for the three techniques for analysis of removal; mass loss, colour change and change in resistance to flow of water, as discussed in 3.5.1-3, as well as additional techniques employed to further understand the mechanisms of removal. As well as being interesting in itself, soaking results are then used as a reference point when samples are subject to mechanical action and hydrodynamics.

5.1. Polyester

5.1.1. Effect of Temperature

Mass, colour and resistance measurements

Figure 5.1 shows the percentage mass removal, increase in L^* (lightness), decrease in a^* (redness) and decrease in resistance for soiled polyester soaked in wash solution containing twice the CMC of LAS at 20, 40 and 60 °C. As expected, it can be seen that removal is lowest at 20 °C, and increases when the temperature is increased to 40 °C and 60 °C. Figure 4.2.4 confirmed that all constituents of sebum have melted when a temperature of 40 °C is reached, therefore it would be expected that the sebum would be molten at 40 °C, and would be fully liquefied at 60 °C. The liquefied sebum at 60 °C will be more accessible for the surfactant leading to overall increased removal.

The percentage mass removal is higher than colour or resistance. It is suspected that some dye may remain on the fabric while sebum and dye are removed leading to the change in colour being less than the other measures. The change in resistance is suspected to be lower than mass removal as the sebum has spread further into the pores of the fabric with help of the surfactant, and at 40 °C and 60 °C the higher temperature will also aid this.

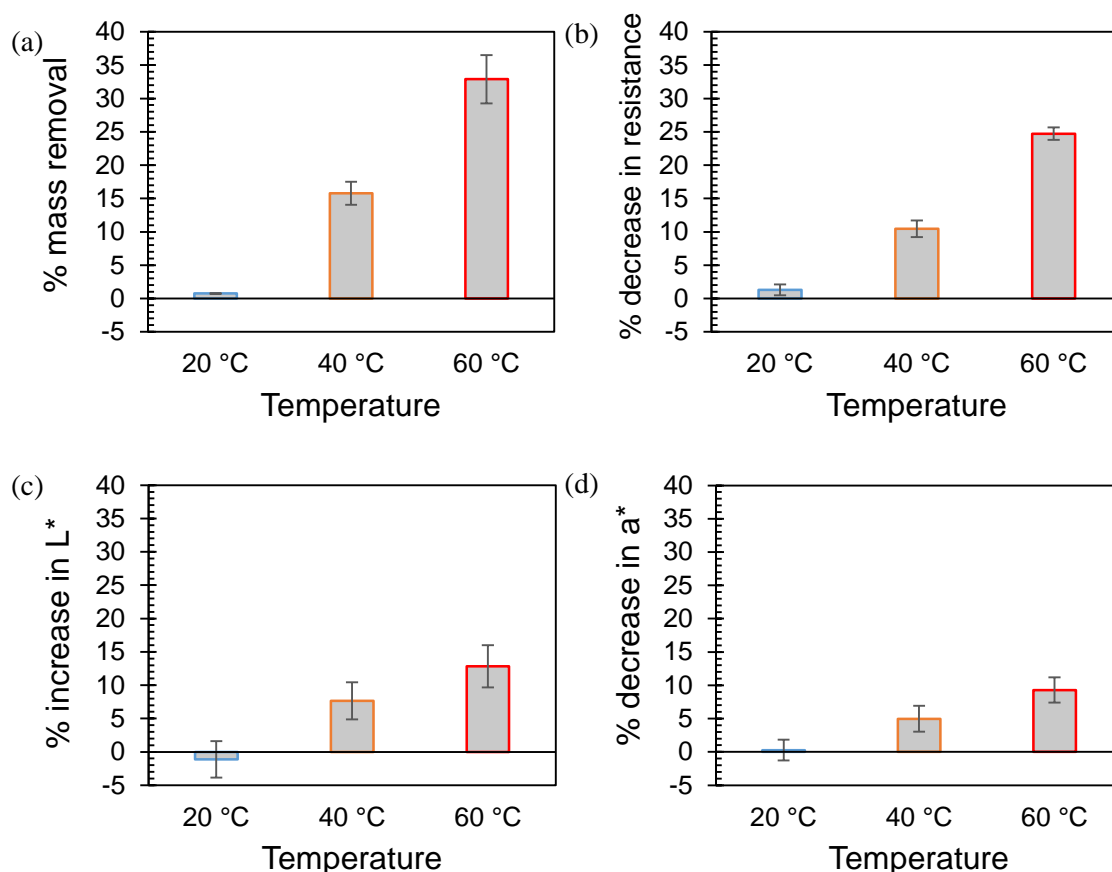


Figure 5.1. Effect of temperature on cleaning by chemical action for polyester soiled with sebum. Surfactant was used at a concentration of 2 x CMC. Cleaning is measured by (a) % mass removal, (b) % decrease in resistance, (c) % increase in L^* and (d) % decrease in a^* . The error bars represent \pm one standard deviation for three fabrics. Five measurements were taken from each fabric for colour and resistance.

Colour of top and underside of fabric

For samples washed at 20 °C and 40 °C the colour change of the back and front are equal, which is to be expected as there should be no reason that the top or underside should be preferentially cleaned. This is not the case for 60 °C, as shown in Figure 5.2. Although increasing removal is seen from the underside of the fabric as the temperature increases, the removal is significantly less than for the front of the fabric. This supports the hypothesis above that some liquefied sebum has soaked into the unoccupied pores.

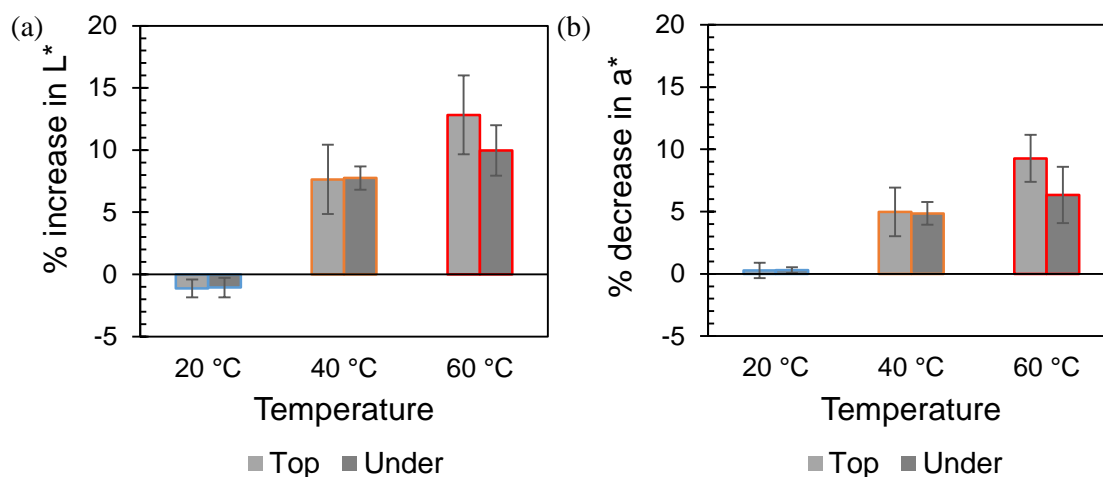


Figure 5.2. Comparison of the colour of the top and underside of polyester soiled with sebum cleaned using chemical action at 20 °C, 40 °C and 60 °C with surfactant at a concentration of 2 x CMC. Colour is measured as (a) L^* and (b) a^* . The error bars represent \pm one standard deviation for three fabrics. Five measurements were taken from each fabric.

Mass per unit area

Figure 5.3 shows the mass per unit area of the fabric at various distances from the central point. The bar above the graph shows the soiled area of the sebum. The mass per unit area of the three central point's supports the mass results found above, where 20 °C is very similar to the fouled polyester, then removal increases for 40 °C and 60 °C. Interestingly, the strip taken adjacent to the fouled area shows increased mass at increased temperature. At higher temperatures the liquefied sebum spreads from the central fouled area onto the clean area of the polyester. It can be seen that the sebum only spreads to the area closest to the fouled strip, and no significant mass change is seen further from the central strip.

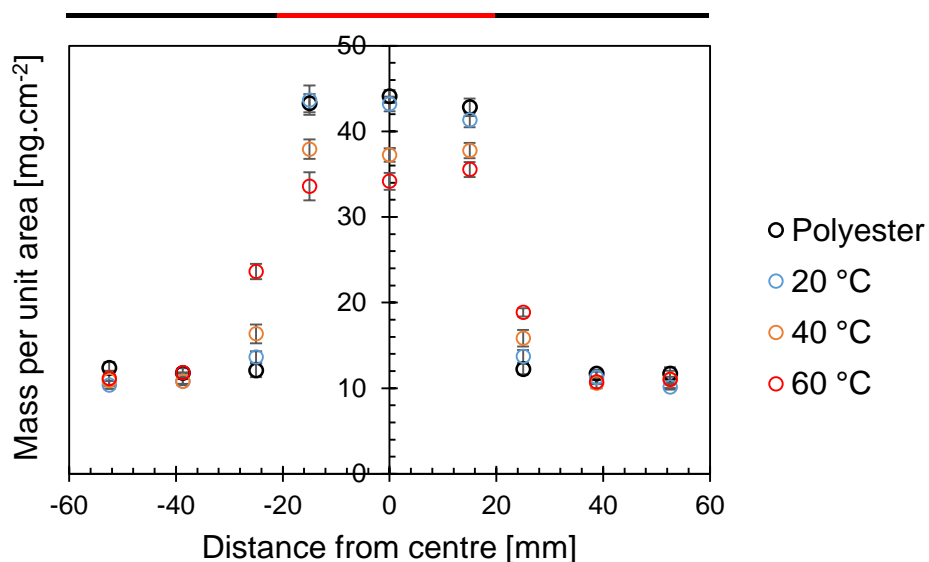


Figure 5.3. Mass per unit area of polyester soiled with sebum cleaned using chemical action at 20 °C, 40 °C and 60 °C with surfactant at a concentration of 2 x CMC. The error bars represent \pm one standard deviation for three fabrics.

FTIR

The FTIR spectrum of both the top and underside of the fabric are shown in Figure 5.4. At all temperatures the FTIR trace is more similar to the soiled polyester than to the virgin polyester, with distinctive sebum peaks at 2915, 2850 and 1180 cm^{-1} . This suggests that there is still a large amount of sebum remaining on the fabric, which supports the mass removal results as they show only 32.9% removal at the highest temperature (Figure 5.1).

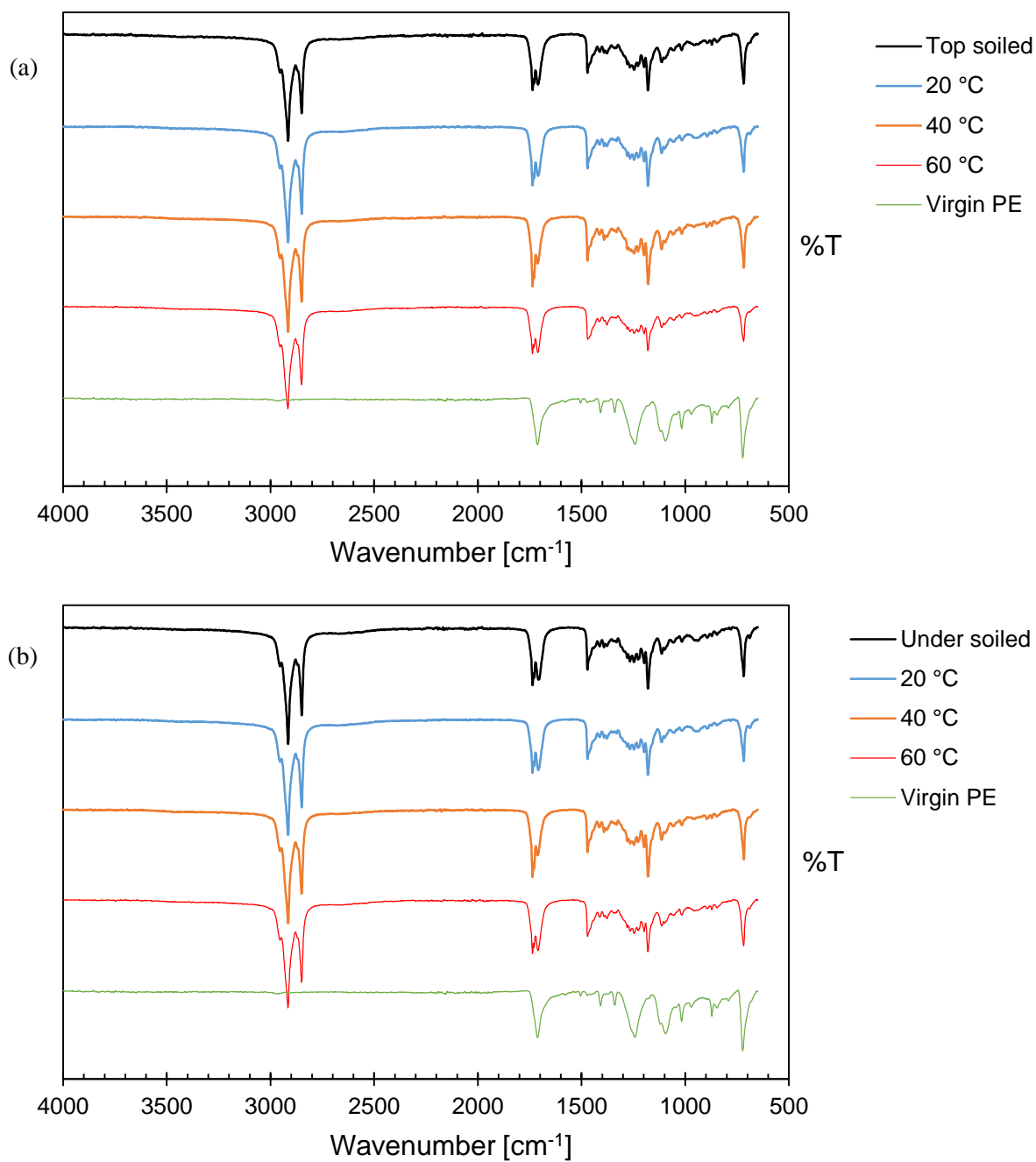


Figure 5.4. FTIR of polyester soiled with sebum cleaned using chemical action at 20 °C, 40 °C and 60 °C with surfactant at a concentration of 2 x CMC. This is compared to soiled and virgin polyester for both the (a) top and (b) underside of the fabric.

5.1.2. Effect of surfactant concentration at 40 °C

Mass, colour and resistance measurements

When fabrics are soaked in 40 °C it can be seen that removal is highest when the surfactant is used at a concentration of 2 times it's CMC when compared to 0.1 times its CMC and water, as shown in Figure 5.1. Using surfactant at 0.1 times its CMC shows no cleaning benefit over soaking in water alone. Colour removal appears to be higher than mass or resistance for these two samples, however error bars show large variation in colour readings, which suggests removal is irregular along the length of the fabric.

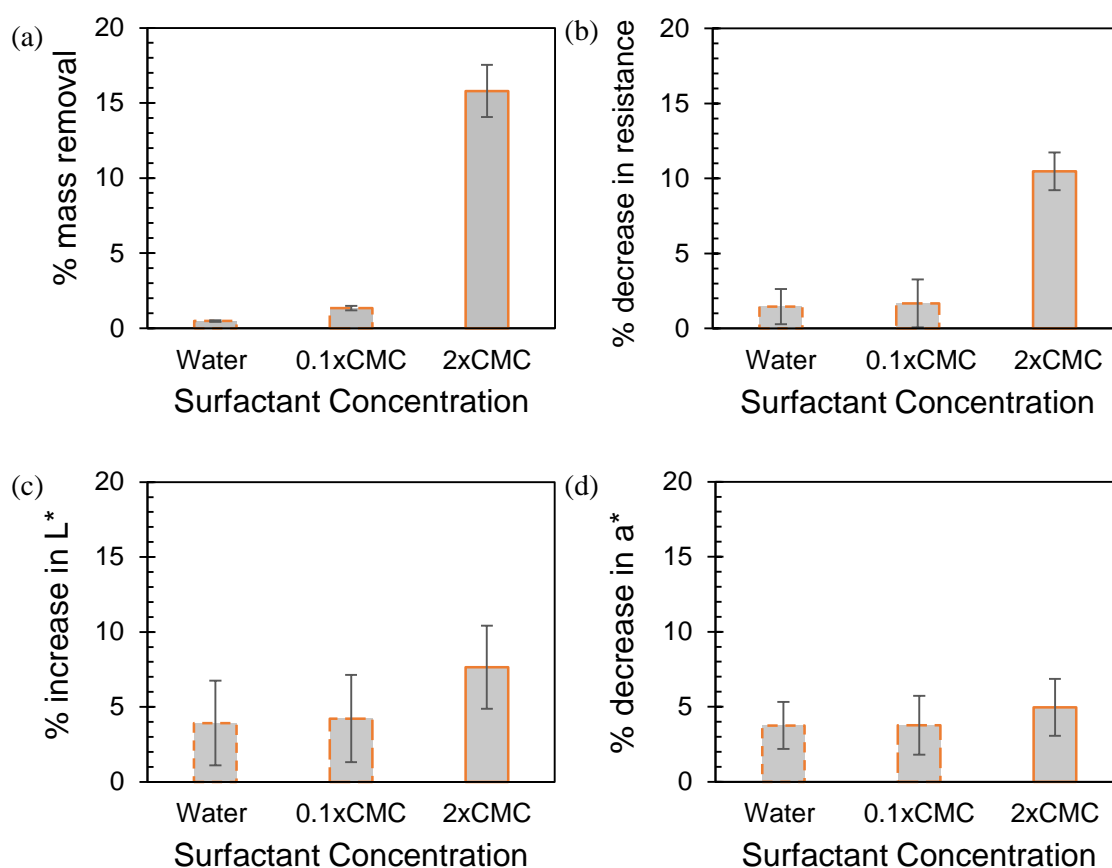


Figure 5.5. Effect of surfactant concentration on cleaning by chemical action at 40 °C for polyester soiled with sebum. Cleaning is measured by (a) % mass removal, (b) % decrease in resistance, (c) % increase in L^* and (d) % decrease in a^* . The error bars represent \pm one standard deviation for three fabrics. Five measurements were taken from each fabric for colour and resistance.

Colour of top and underside of fabric

The colour of the top and underside suggest removal is even from both sides of the fabric when polyester is soaked in the three different wash solutions, as shown in Figure 5.6. This is what would be expected from soaking as there is no additional treatment or action on a particular side of the fabric.

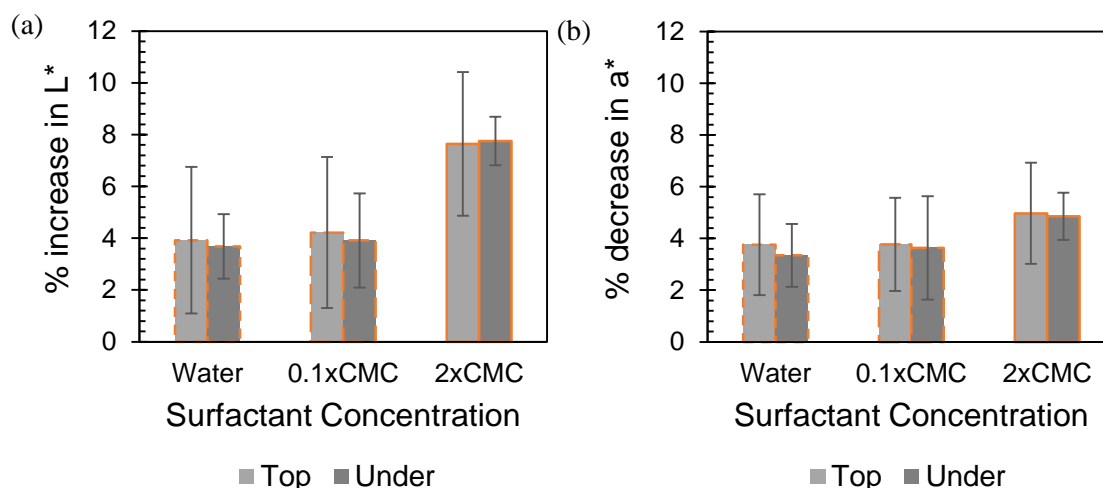


Figure 5.6. Comparison of the colour of the top and underside of polyester soiled with sebum cleaned using chemical action at 40 °C with water and surfactant at a concentration of 0.1 x and 2 x CMC. Colour is measured as (a) L* and (b) a*. The error bars represent \pm one standard deviation for three fabrics. Five measurements were taken from each fabric.

Mass per unit area

Figure 5.7 shows the mass per unit area measurements of the fabrics. This shows that water and 0.1 times the CMC of the surfactant both have a very similar mass profile to the soiled polyester, other than a slight decrease in mass at the edge of the soiled area on the fabric, and slight increase in mass at the clean area adjacent to this, indicating some spreading occurs even though mass removal is small. The mass of the soiled strip of the fabric soaked in 2 times the CMC of the surfactant shows a significant decrease in mass when compared to the soiled polyester. These fabrics also see additional spreading of sebum to the adjacent area.

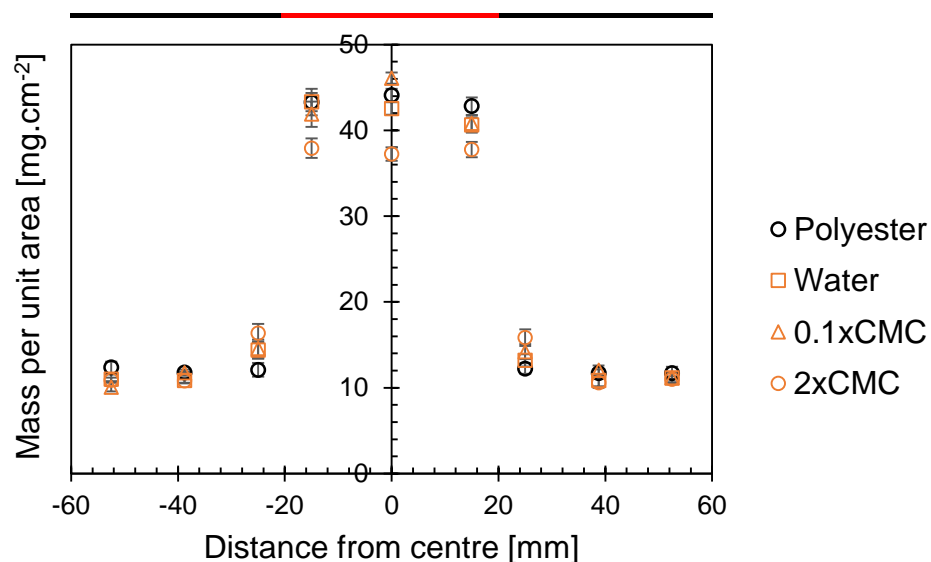


Figure 5.7. Mass per unit area of polyester soiled with sebum cleaned using chemical action at 40 °C with water and surfactant at a concentration of 0.1 x and 2 x CMC. The error bars represent \pm one standard deviation for three fabrics.

FTIR

When FTIR spectra, Figure 5.8, are examined it can be seen that for all three wash solutions the spectrum is much more similar to that of soiled polyester than virgin polyester. The characteristic peaks of sebum can still be clearly seen on all three cleaned samples. Again, this is in line with the low removal seen by soaking alone.

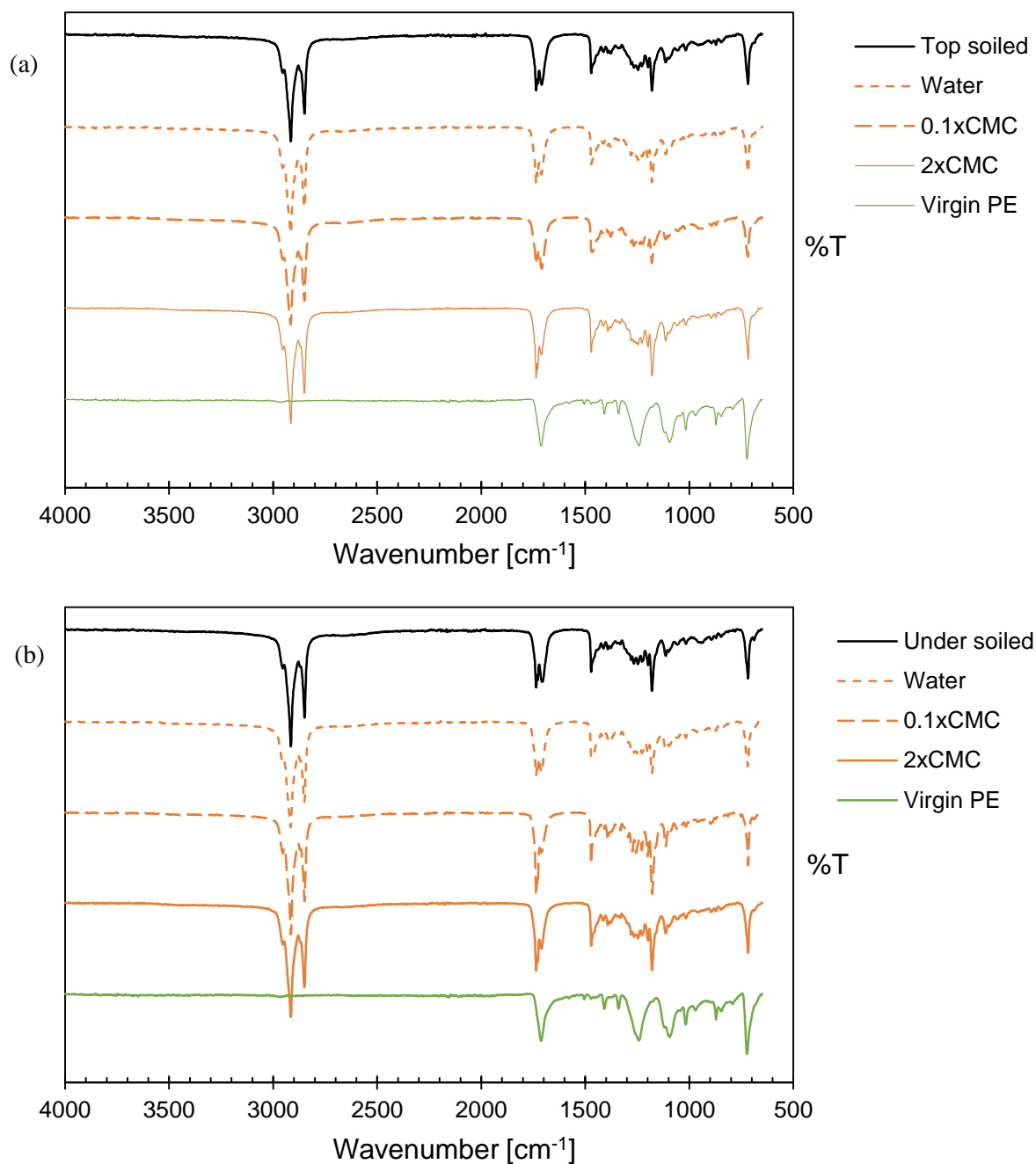


Figure 5.8. FTIR of polyester soiled with sebum cleaned using chemical action at 40 °C with water and surfactant at a concentration of 0.1 x and 2 x CMC. This is compared to soiled and virgin polyester for both the (a) top and (b) underside of the fabric.

Zeta Potential

Figure 5.9 shows the zeta potential of fabrics washed under these three conditions, and compares this to virgin and soiled polyester. It was hypothesised that the soaked fabrics would occupy the space in between the virgin and soiled fabrics on the graph, getting closer to the virgin polyester with

increased cleaning. Instead the soaked fabrics have a zeta potential less negative than both the virgin and soiled polyester. This is the case for fabrics soaked in surfactant and water therefore the effect must be due to soaking in water.

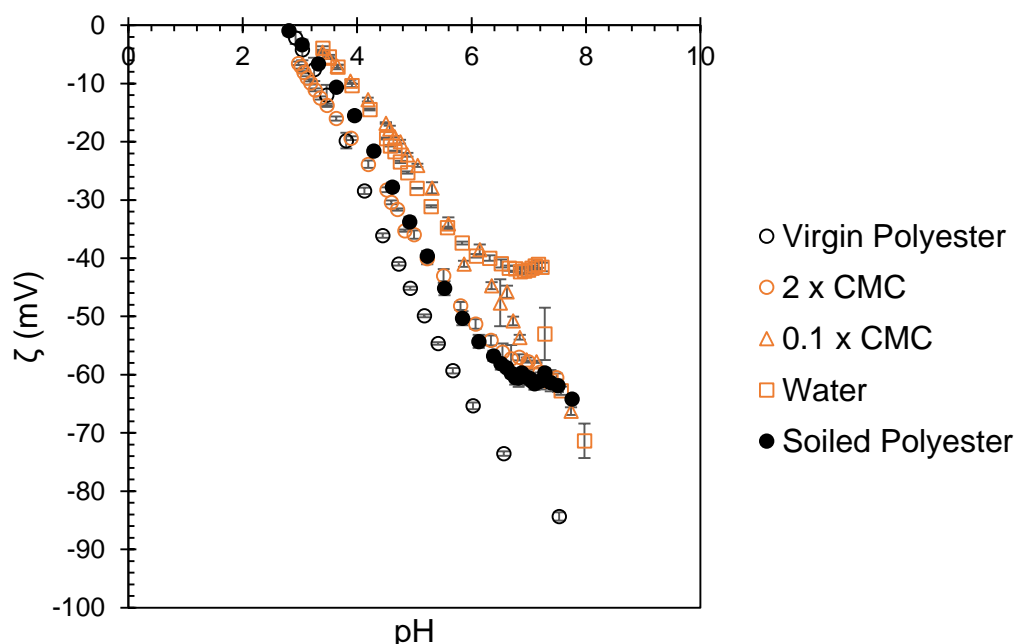


Figure 5.9. Effect of surfactant concentration on zeta potential for polyester soiled with sebum and cleaned using chemical action at 40 °C. The error bars represent \pm one standard deviation for four repeat measurements taken on each fabric.

The question was raised as to whether the change in zeta potential was due to the effect of soaking on the sebum or on the polyester itself. For this reason virgin polyester was soaked under the same conditions and the zeta potential measured, as shown in Figure 5.10. It can be seen that the soaking of virgin polyester actually shifted the zeta potential more negative therefore it can be concluded that the change in zeta potential of the soiled polyester samples after soaking is due to an interaction between the sebum and the 40 °C water during soaking. It is suspected that this is swelling of the soil layer. The shift in zeta potential of the soaked virgin polyester may be due to absorption of water by the polyester fibres, or some interaction between the water and any residual coating or detergent from desizing remaining of the polyester.

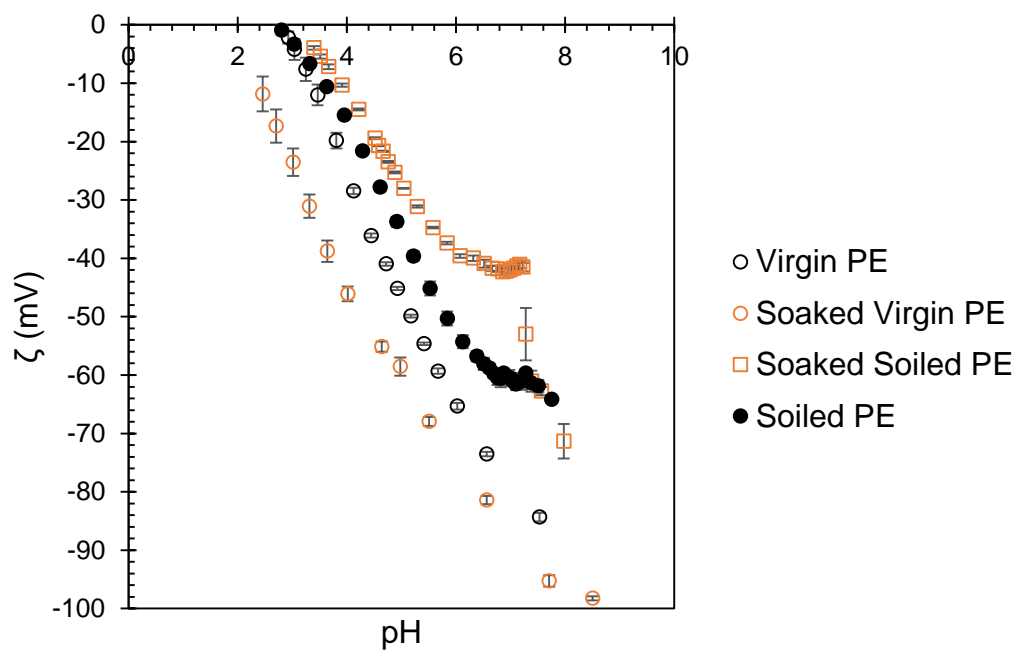


Figure 5.10. Zeta potential of virgin and soiled polyester fabrics soaked in 40 °C water. The error bars represent \pm one standard deviation for four repeat measurements taken on each fabric.

Since a difference is found between virgin polyester and soaked virgin polyester in terms of surface charge, it was also of interest to investigate whether a difference could be seen by FTIR. Figure 5.11 shows that there is no difference between virgin polyester and soaked virgin polyester in terms of chemical bonds present on the surface.

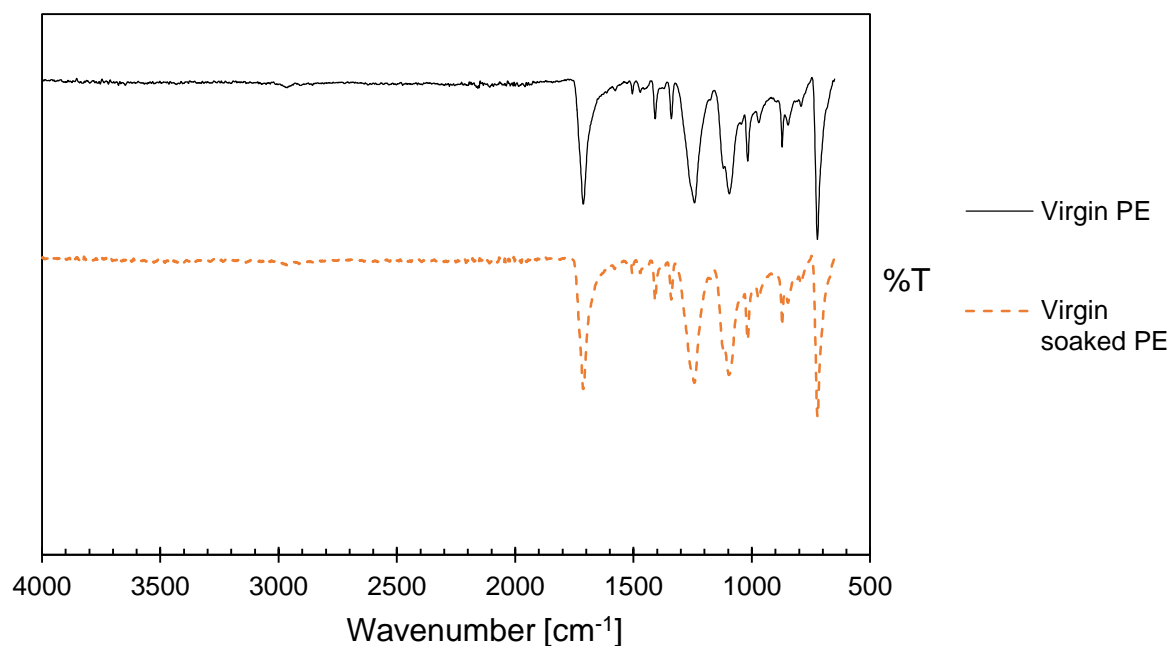


Figure 5.11. FTIR of virgin polyester soaked in at water at 40 °C compared to virgin polyester.

5.1.3. Effect of surfactant concentration at 20 °C

Mass, colour and resistance measurements

Figure 5.12 shows the change in mass colour and resistance for fabrics soaked in 20 °C wash solution with various levels of surfactant. It can be seen that removal is very low for all three conditions, with 2 x CMC giving a very small but not meaningful benefit. For all three samples lightness (L^*) decreases suggesting the fabric is more dirty than the soiled sample, although the percentage change is so very low so this would not be a meaningful difference. This could be caused by some change in the sebum after soaking in water, a change that is not seen at other temperatures as it is masked by increased removal.

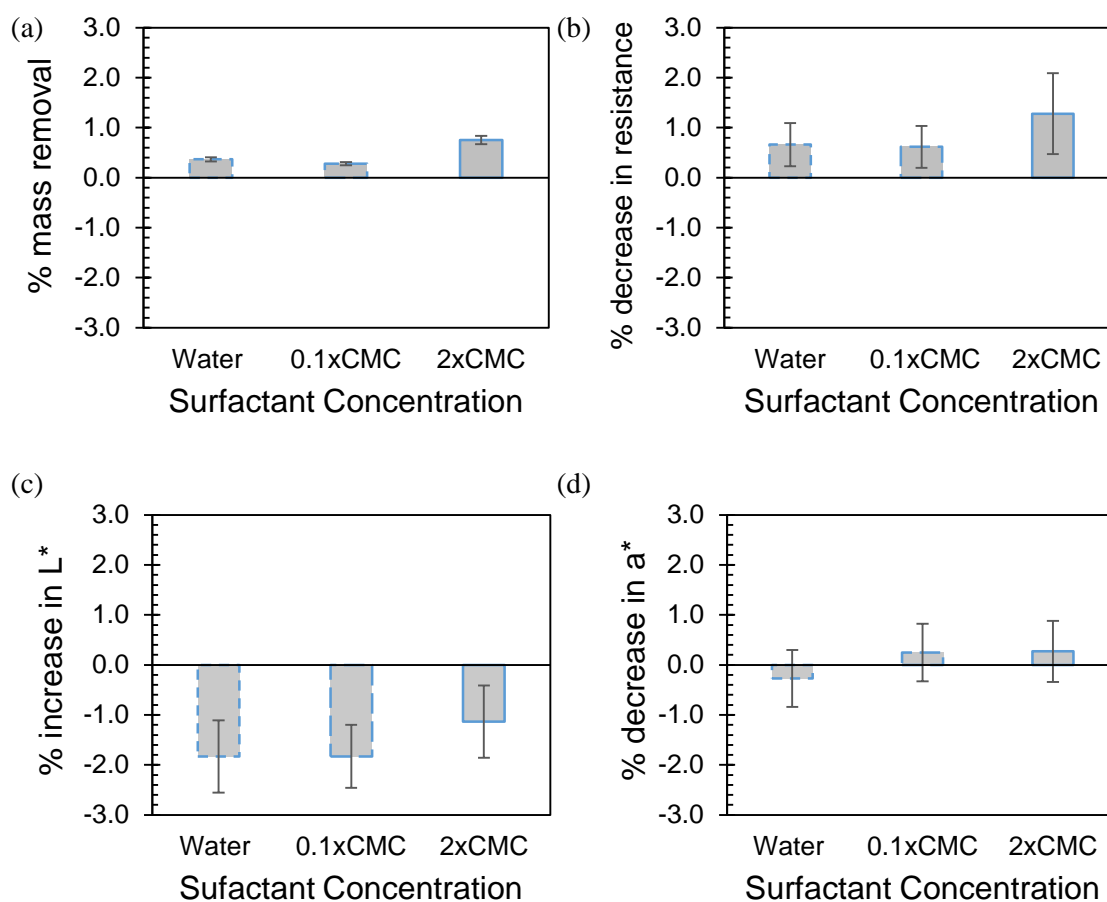


Figure 5.12. Effect of surfactant concentration on chemical action at 20 °C for polyester soiled with sebum. Cleaning is measured by (a) % mass removal, (b) % decrease in resistance, (c) % increase in L^* and (d) % decrease in a^* . The error bars represent \pm one standard deviation for three fabrics. Five measurements were taken from each fabric for colour and resistance.

Colour of top and underside of fabric

As expected, Figure 5.13 shows that removal from the top and underside of the fabric is similar, and shows that only a very small change is seen in the colour of all three fabrics.

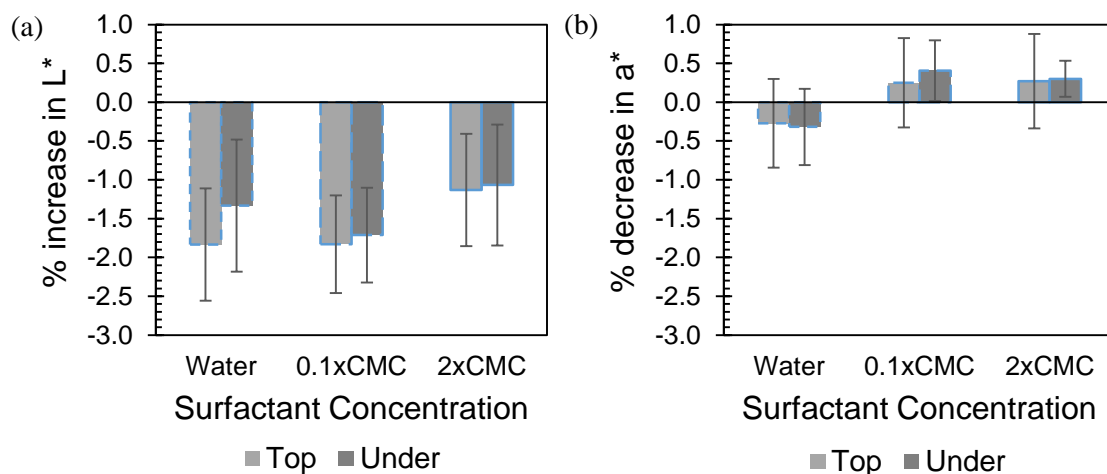


Figure 5.13. Comparison of the colour of the top and underside of polyester soiled with sebum cleaned using chemical action at 20 °C with water and surfactant at a concentration of 0.1 x and 2 x CMC. Colour is measured as (a) L^* and (b) a^* . The error bars represent \pm one standard deviation for three fabrics. Five measurements were taken from each fabric.

Mass per unit area

The mass per unit area measurements, shown in Figure 5.14, shows that all three samples are very similar to the mass profile of soiled polyester. The most removal can be seen from the very central strip of the fouled area, although the mass change is small. The mass of the strip adjacent to the soiled area doesn't show a significant increase in mass, as seen with soaking at 40 °C and 60 °C, which is likely to be due to the fact that the sebum isn't molten at 20 °C.

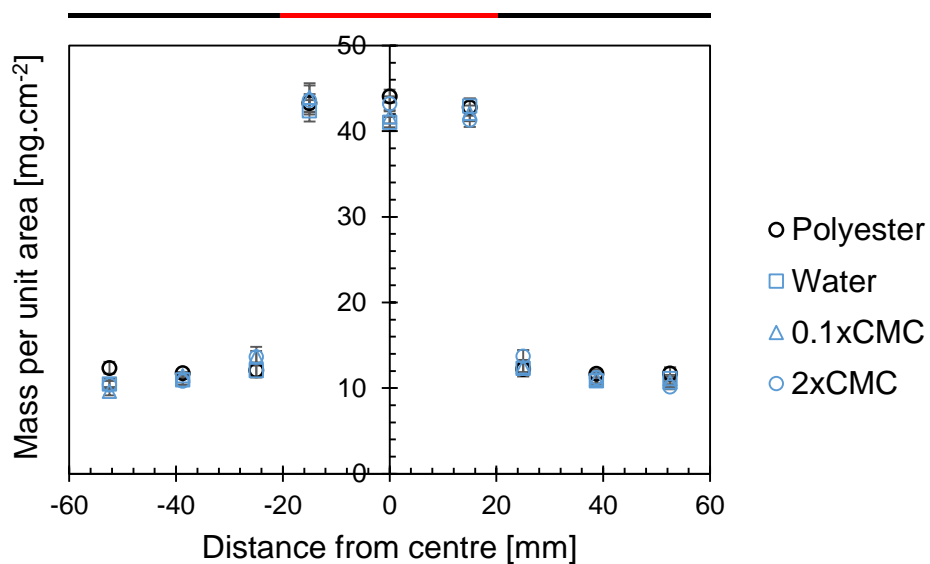


Figure 5.14. Mass per unit area of polyester soiled with sebum cleaned using chemical action at 20 °C with water and surfactant at a concentration of 0.1 x and 2 x CMC. The error bars represent \pm one standard deviation for three fabrics.

FTIR

The FTIR of samples soaked in 20 °C wash solution, Figure 5.15, shows very little differences of both the top and underside of the fabric when compared to soiled polyester. This is in line with the low removal results by soaking at 20 °C.

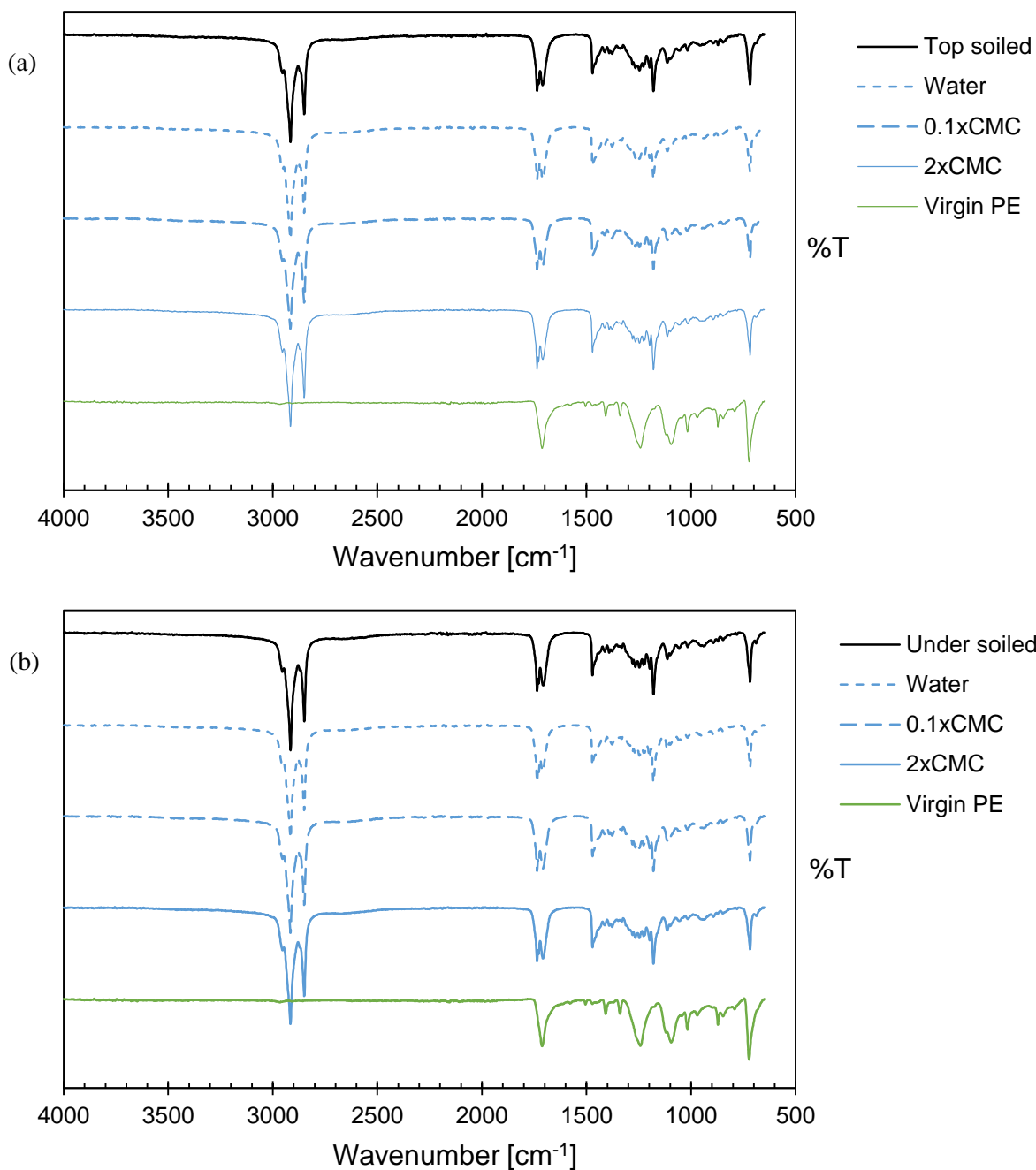


Figure 5.15. FTIR of polyester soiled with sebum cleaned using chemical action at 20 °C with water and surfactant at a concentration of 0.1 x and 2 x CMC. This is compared to soiled and virgin polyester for both the (a) top and (b) underside of the fabric.

SEM

Soaked fabric looks very similar to soiled fabric under SEM, as shown in Figure 5.16. At x20 magnification the sebum appears more embedded into the yarn when compared with the soiled fabric (Figure 4.21), although the difference is small. This suggests that soaking allows the sebum to better

penetrate the yarns. The x100 image supports this, as when compared to the soiled fabric in Figure 4.21, the soaked image appears to contain less loose uncoated fibres. The x500 image shows sebum both coating individual fibres and forming bridges between adjacent fibres, similar to the soiled image. The images support the previous finding that soaking alone at low temperature does not cause significant removal. This is likely to cause the decrease in lightness of both the topside and underside of the fabric.

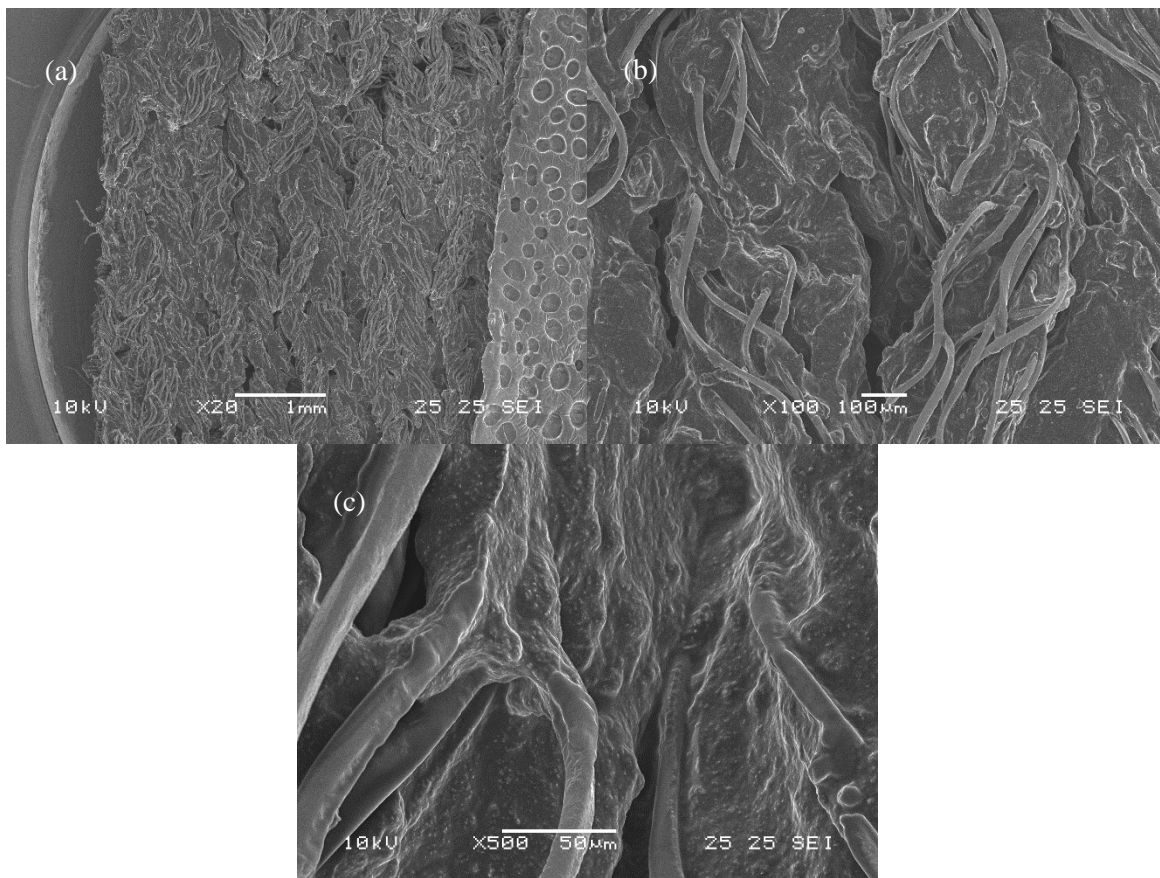


Figure 5.16. SEM images of soiled polyester soaked in 20 °C 2 x CMC surfactant solution at (a) x20 (b) x100 and (c) x500 magnifications.

5.2. Cotton

5.2.1. Effect of Temperature

Mass, colour and resistance measurements

As seen previously with polyester, removal of sebum from cotton can also be seen to increase as temperature is increased, as shown in Figure 5.17. However, unlike polyester, removal of sebum from cotton fabric at 60 °C is much higher than the other temperatures, and is well over 50% on all four measures. When cotton fabric is placed in 60 °C water with surfactant at 2 times the CMC it is observed that the sebum lifts straight from the surface of the fabric and collects at the air-water interface. It is likely to be due to the fact that sebum is fully liquefied at 60 °C, as observed with DSC in Section 4.2.4, and as such is easily removed in 60 °C surfactant solution. This is not the case for polyester, which contains more sebum than cotton. Polyester has $32.30 \pm 1.61 \text{ mg.cm}^{-2}$ of sebum compared to $9.687 \pm 0.49 \text{ mg.cm}^{-2}$ on cotton, and the layer of sebum is more embedded into the polyester. The decrease in resistance of the fabric washed in 40 °C surfactant solution is much higher than the reduction in mass; this suggests that sebum has been removed from the pores. For polyester it was found that removal as quantified by colour change was less than mass change, however it can be seen that removal from colour change is approximately equal to (L^*) or slightly above (a^*) mass removal for 20 °C and 40 °C. This suggests sebum has been redistributed on the fabric rather than being fully removed.

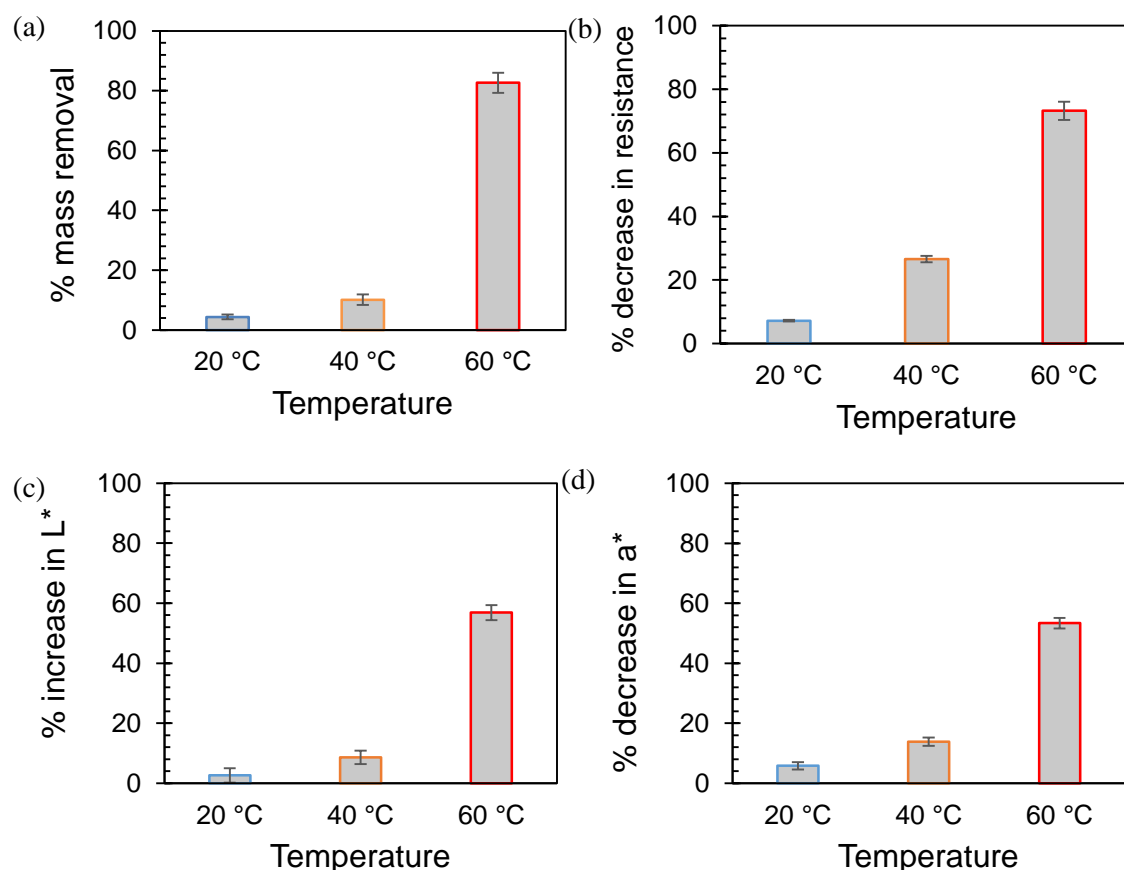


Figure 5.17. Effect of temperature on chemical action for cotton soiled with sebum. Surfactant was used at a concentration of 2 x CMC. Cleaning is measured by (a) % mass removal, (b) % decrease in resistance, (c) % increase in L^* and (d) % decrease in a^* . The error bars represent \pm one standard deviation for three fabrics. Five measurements were taken from each fabric for colour and resistance.

Colour of top and underside of fabric

For 60 °C removal of sebum from the topside and underside is similar, which is to be expected as, without mechanical action, there is no reason for preferential removal from either side. However, interestingly, removal from the underside of cotton washed at 40 °C is significantly less than removal from the top surface. It is suspected that this is due to the fact that there is significantly less sebum on the underside of cotton, as shown in Figure 3.4, and since both sides of the fabric are subject to the same conditions when soaking alone is used for cleaning some sebum may penetrate deeper into the fabric when it is slightly molten. The results are more similar for 20 °C, only showing a small difference between the back and front of the fabric, suggesting this mechanism may also occur, but to a much lesser extent.

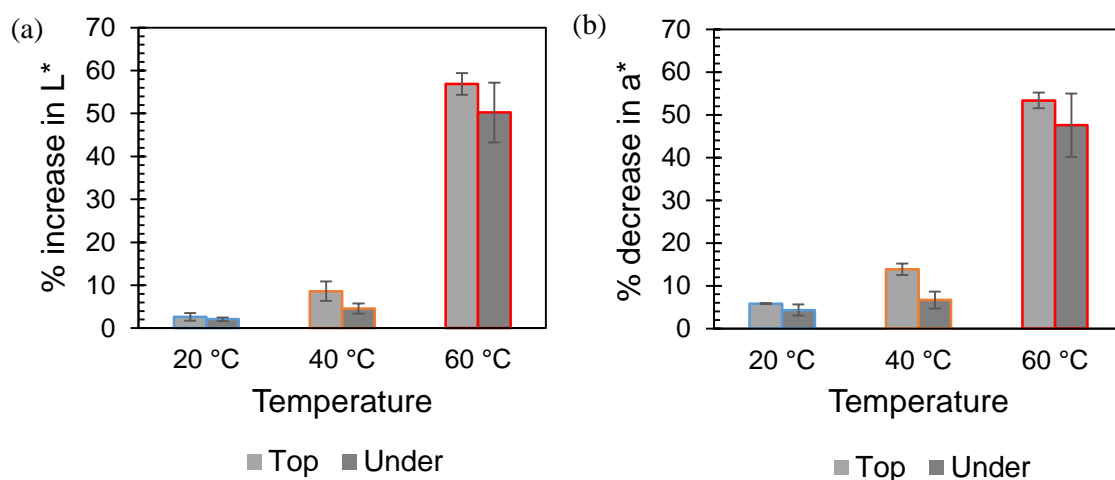


Figure 5.18. Comparison of the colour of the top and underside of cotton soiled with sebum cleaned using chemical action at 20 °C, 40 °C and 60 °C with surfactant at a concentration of 2 x CMC. Colour is measured as (a) L* and (b) a*. The error bars represent \pm one standard deviation for three fabrics. Five measurements were taken from each fabric.

Mass per unit area

Mass per unit area results, Figure 5.19, show the mass of the central soiled strip is significantly reduced, almost to the level of virgin cotton, for fabrics soaked in 60 °C wash solution. A smaller but still significant reduction is seen for 40 °C, while fabrics soaked at 20 °C are very similar to soiled cotton. The mass of the area adjacent to the soiled strip shows a small increase in mass for 40 °C, but not to the same extent that was seen for polyester, therefore it can be concluded that cotton doesn't allow the sebum to spread in the same way that polyester does.

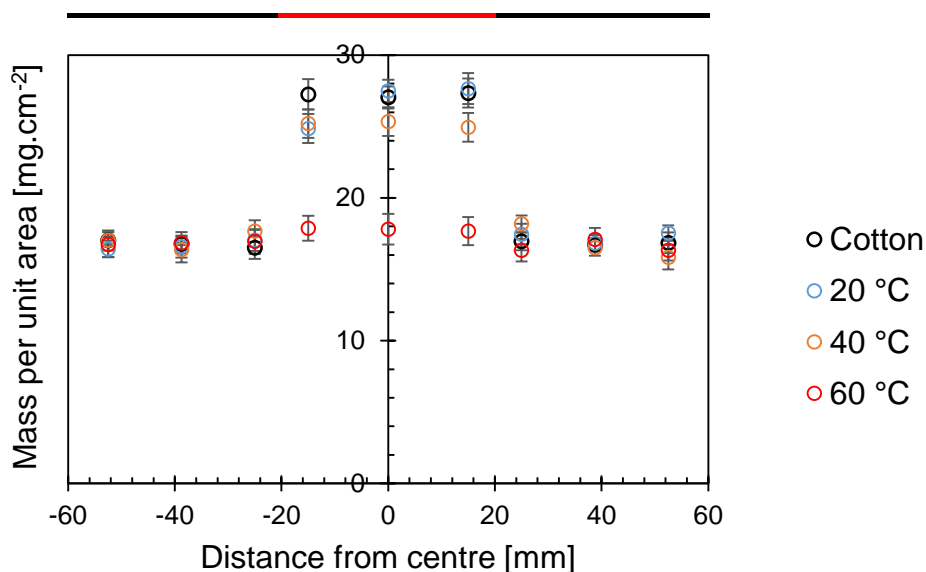


Figure 5.19. Mass per unit area of cotton soiled with sebum cleaned using chemical action at 20 °C, 40 °C and 60 °C with surfactant at a concentration of 2 x CMC. The error bars represent \pm one standard deviation for three fabrics.

FTIR

Figure 5.20 shows the FTIR spectra of the fabrics soaked in surfactant solution at the three different temperatures as well as soiled cotton and virgin cotton. On the top surface (a) it can be seen that the characteristic double peak of cotton at 3339 and 3273 cm^{-1} is somewhat masked by the soiled cotton and the fabrics soaked at the two lower temperatures, whereas the same peaks are much more visible on fabric washed at 60 °C. Conversely the sebum peaks at 2882 and 2852 cm^{-1} are very pronounced on the samples washed at the two lower temperatures, whereas at the higher temperature this peak has significantly reduced in size. Similar observations can be made over the entire spectrum. When the underside of the fabric is considered again the cotton peaks become more visible and the sebum peaks appear reduced when comparing the 20 °C and 60 °C fabrics. However, the 40 °C experiment shows stronger sebum peaks, for example at 2971 and 2841 cm^{-1} , which supports the hypothesis that soaking at 40 °C is aiding transport of sebum through the pores of the cotton.

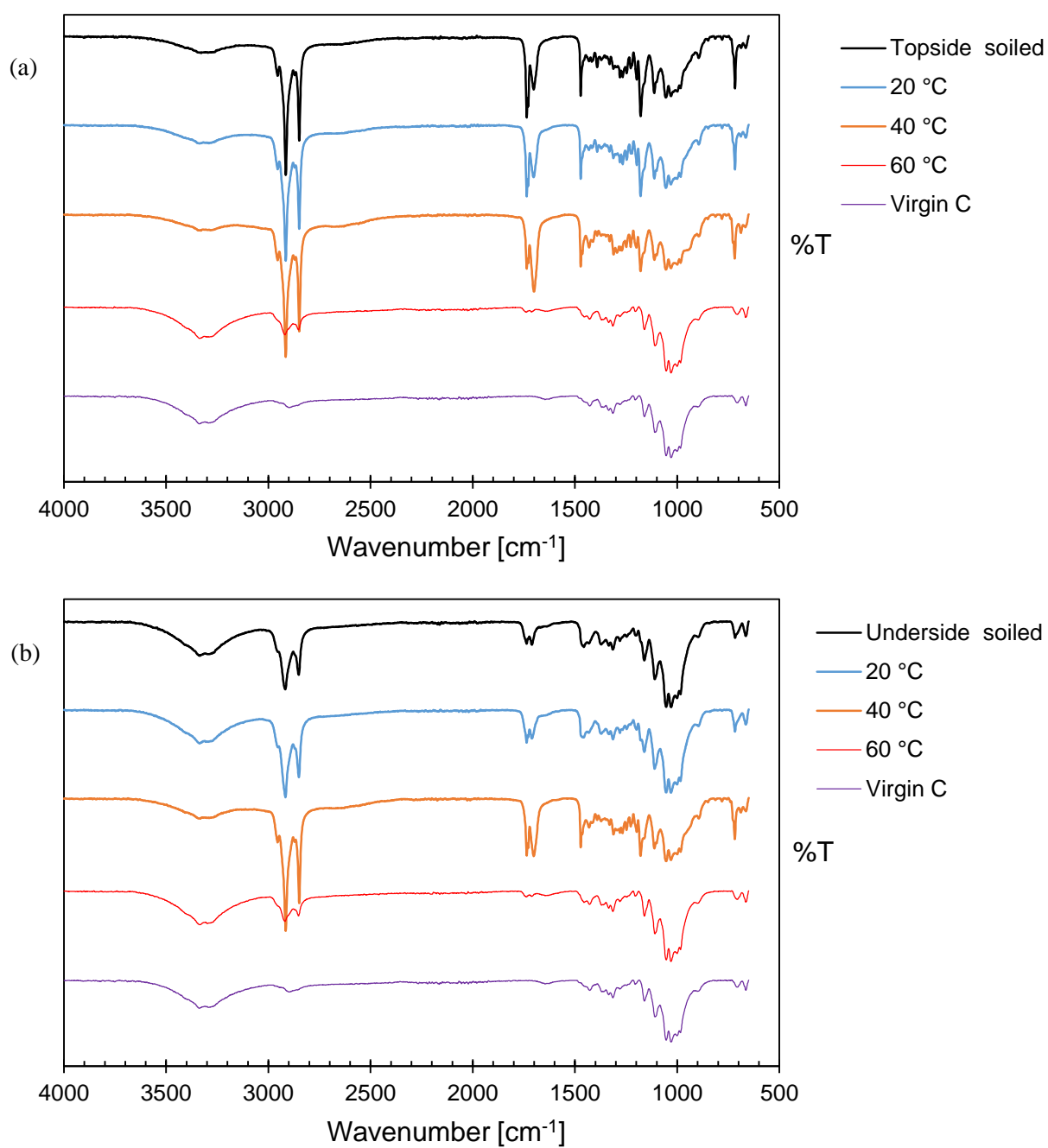


Figure 5.20. FTIR of cotton soiled with sebum cleaned using chemical action at 20 °C, 40 °C and 60 °C with surfactant at a concentration of 2 x CMC. This is compared to soiled and virgin cotton for both the (a) top and (b) underside of the fabric.

5.2.2. Effect of surfactant concentration at 40 °C

Mass, colour and resistance measurements

Figure 5.21 shows that using surfactant at two times the CMC gives a cleaning benefit, however using it at 0.1 times the CMC gives no benefit over water alone when soaking at 40 °C. The decrease in resistance is higher than the decrease in mass for all three fabrics. This suggests that at this temperature with all three wash solutions the water is penetrating the pores and aiding removal of the molten sebum. The increase is much larger for the surfactant at twice its CMC, which highlights the importance of surfactant concentration when soaking alone is use to clean fabrics.

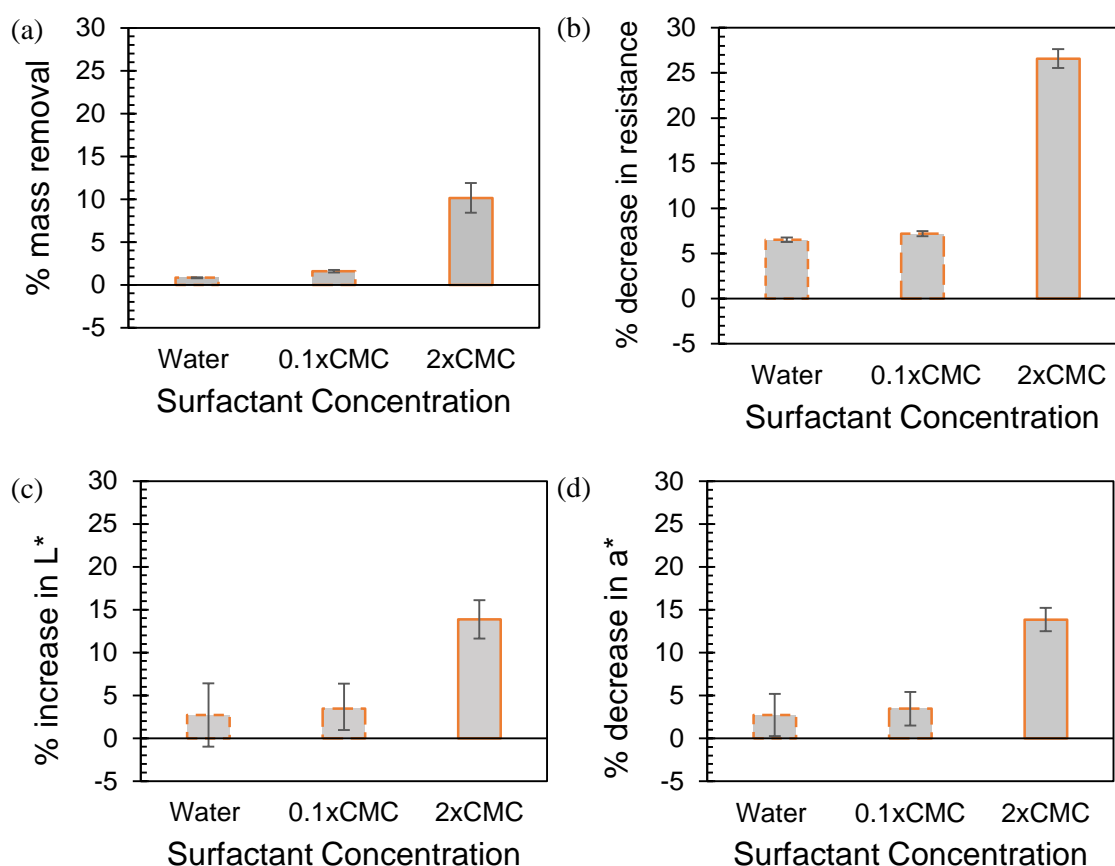


Figure 5.21. Effect of surfactant concentration on chemical action at 40 °C for cotton soiled with sebum. Cleaning is measured by (a) % mass removal, (b) % decrease in resistance, (c) % increase in L^* and (d) % decrease in a^* . The error bars represent \pm one standard deviation for three fabrics. Five measurements were taken from each fabric for colour and resistance.

Colour of top and underside of fabric

When the colour of the topside is compared to the underside, Figure 5.22, it is observed that less sebum is removed from the underside compared to the topside. This effect seems to be much more pronounced for the fabric washed in twice the CMC of the surfactant, suggesting the surfactant is aiding penetration of the fabric by the sebum.

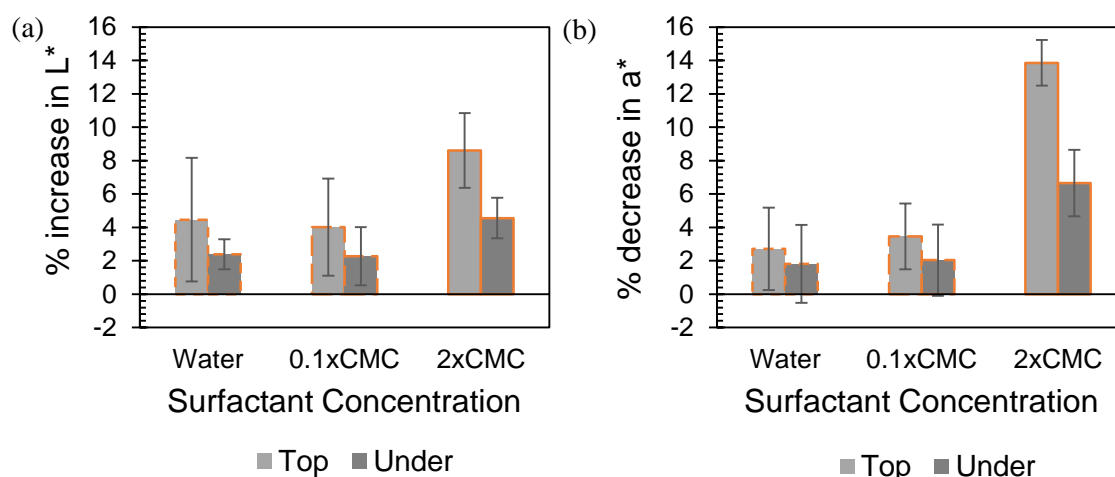


Figure 5.22. Comparison of the colour of the top and underside of cotton soiled with sebum cleaned using chemical action at 40 °C with water and surfactant at a concentration of 0.1 x and 2 x CMC. Colour is measured as (a) L* and (b) a*. The error bars represent \pm one standard deviation for three fabrics. Five measurements were taken from each fabric.

Mass per unit area

The profile of mass per unit area for the three wash conditions is very similar to that of soiled cotton, as shown in Figure 5.23. A small difference is seen in the sample soaked in twice the CMC of the surfactant. The central strip is reduced in mass, whereas a slight increase can be seen in the mass of the adjacent strip of this sample.

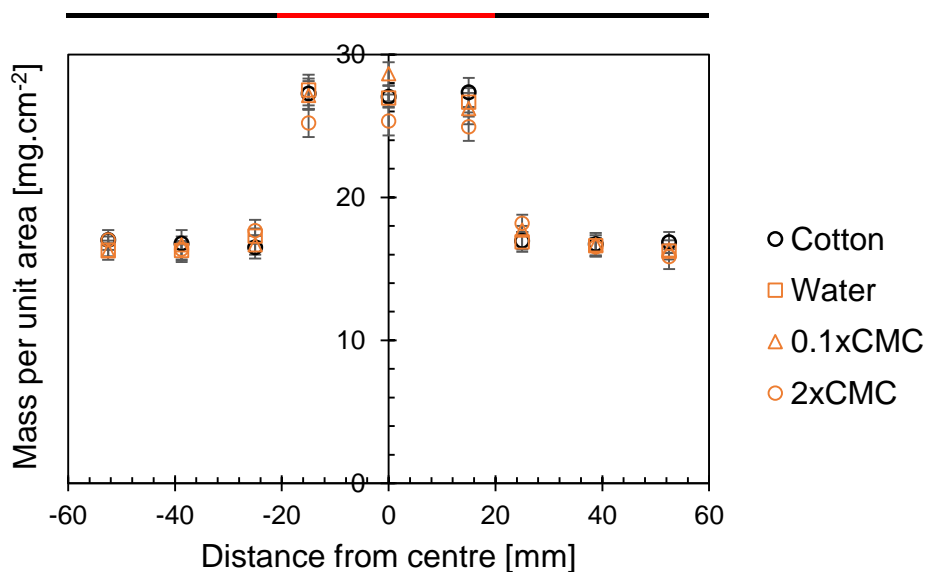


Figure 5.23. Mass per unit area of cotton soiled with sebum cleaned using chemical action at 40 °C with water and surfactant at a concentration of 0.1 x and 2 x CMC. The error bars represent \pm one standard deviation for three fabrics. Five measurements were taken from each fabric.

FTIR

Figure 5.24 (a) shows that the topside of cotton soaked in 40 °C wash solution does not change the chemical makeup of the surface significantly. The sebum somewhat masks the cotton peaks at 3328 and 3271 cm^{-1} , and characteristic sebum peaks can be clearly seen at all levels of surfactant. On the underside of the fabric water and 0.1 times the CMC of the surfactant show very little difference when compared to the soiled surface. On the other hand, when twice the CMC of the surfactant is used the sebum peaks become more pronounced, which supports the hypothesis that sebum has travelled through the pores of the fabric.

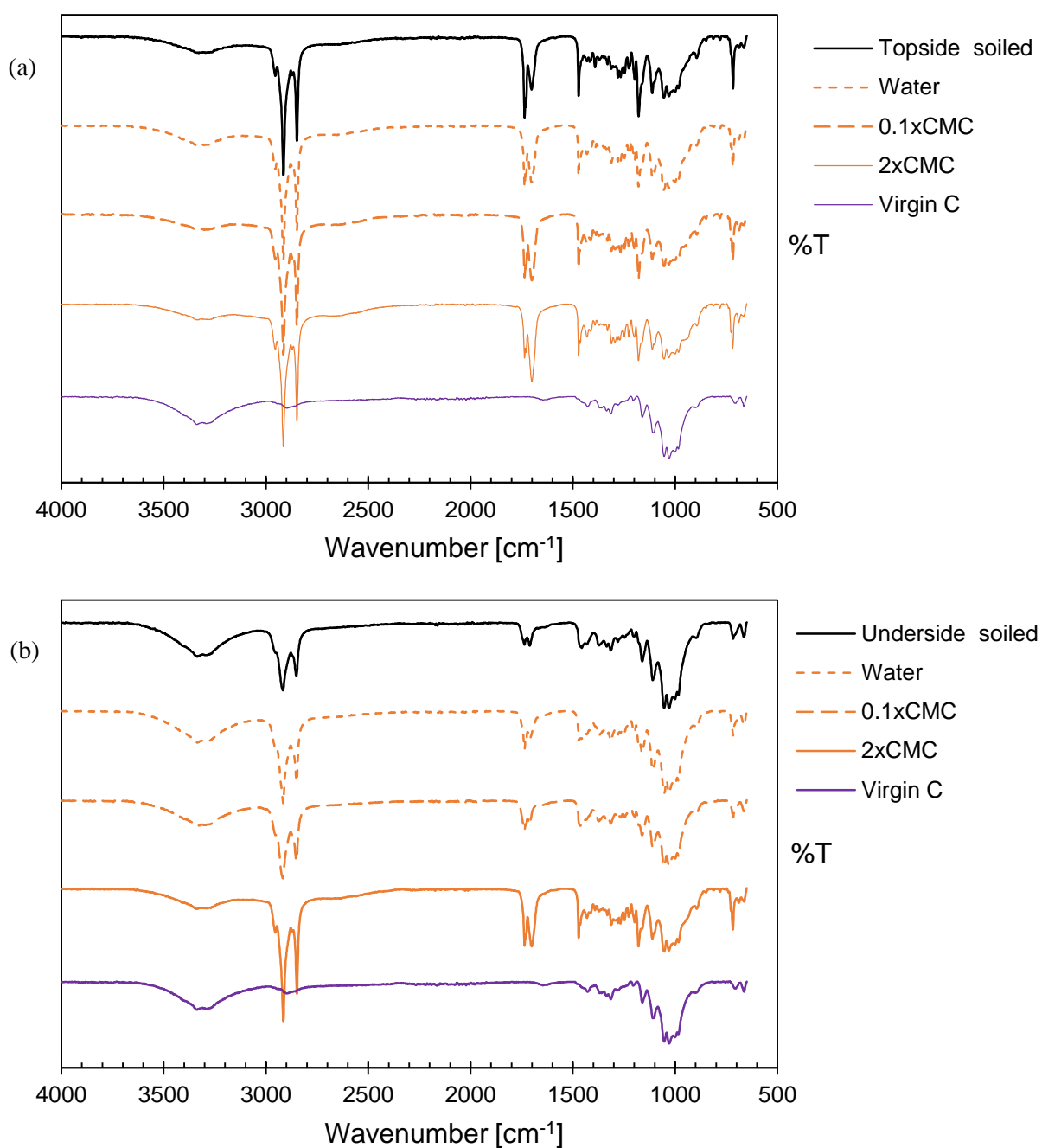


Figure 5.24. FTIR of cotton soiled with sebum cleaned using chemical action at 40 °C with water and surfactant at a concentration of 0.1 x and 2 x CMC. This is compared to soiled and virgin cotton for both the (a) top and (b) underside of the fabric.

Zeta Potential

Unlike polyester, the zeta potential results for cotton are as predicted, as shown in Figure 5.25. The zeta potential data for all three wash solutions lies between the values obtained for virgin cotton and

soiled cotton, with the most cleaned fabric (2 x CMC) being most similar to virgin cotton. This supports other measures of removal presented earlier.

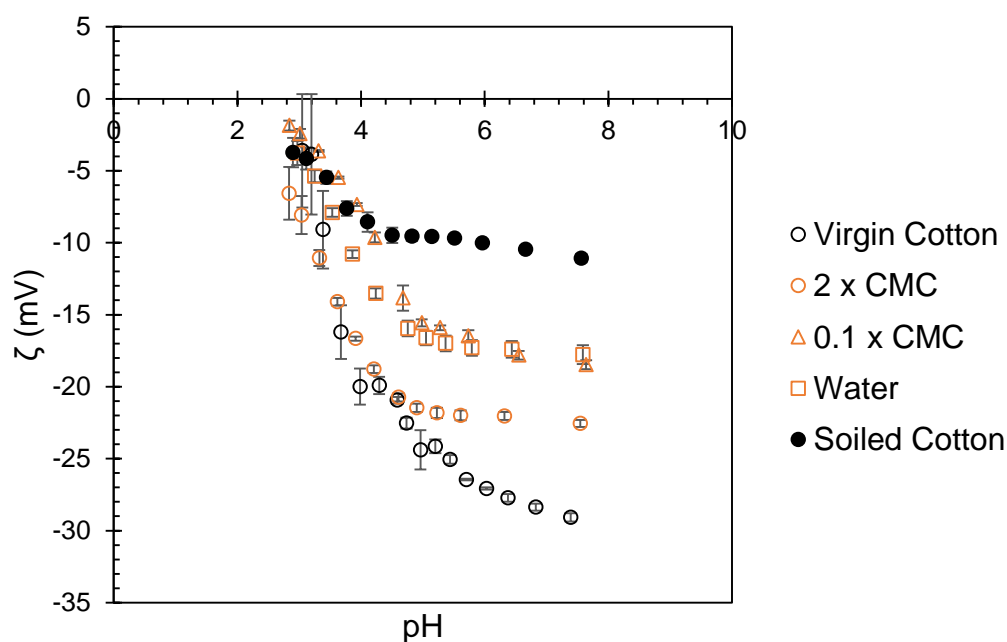


Figure 5.25. Effect of surfactant concentration on zeta potential for cotton soiled with sebum and cleaned using chemical action at 40 °C. The error bars represent \pm one standard deviation for four repeat measurements taken on each fabric.

The zeta potential of soaked virgin cotton was also obtained to allow investigation of the effect of soaking on the cotton, and can be seen in Figure 5.26. Soaked virgin cotton actually decreases the negative zeta potential data further, indicating that the effect of soaking in water has changed the surface charge on the fabric. This could be due to absorption of water on the cotton.

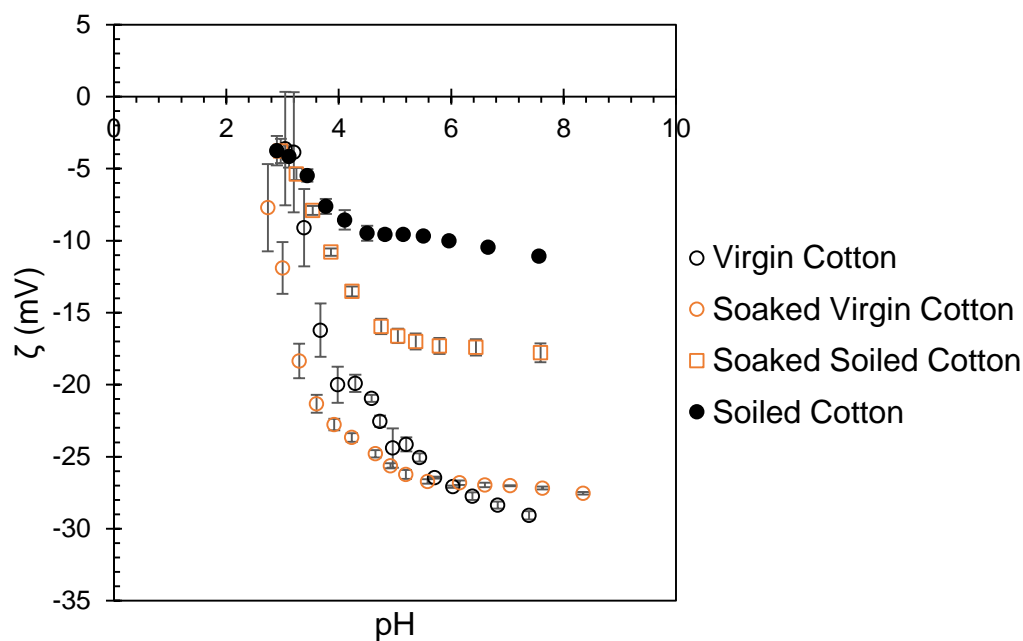


Figure 5.26. Comparing the zeta potential of virgin and soiled cotton fabrics soaked in 40 °C water. The error bars represent \pm one standard deviation for four repeat measurements taken on each fabric.

Soaked virgin cotton was also analysed by FTIR to compare the chemical makeup of the surface to virgin cotton, as shown in Figure 5.27, to see if this has caused the change in surface charged observed above. It can be seen that there is no difference between the soaked and virgin cottons; therefore soaking does not change the chemical makeup of the surface of the cotton.

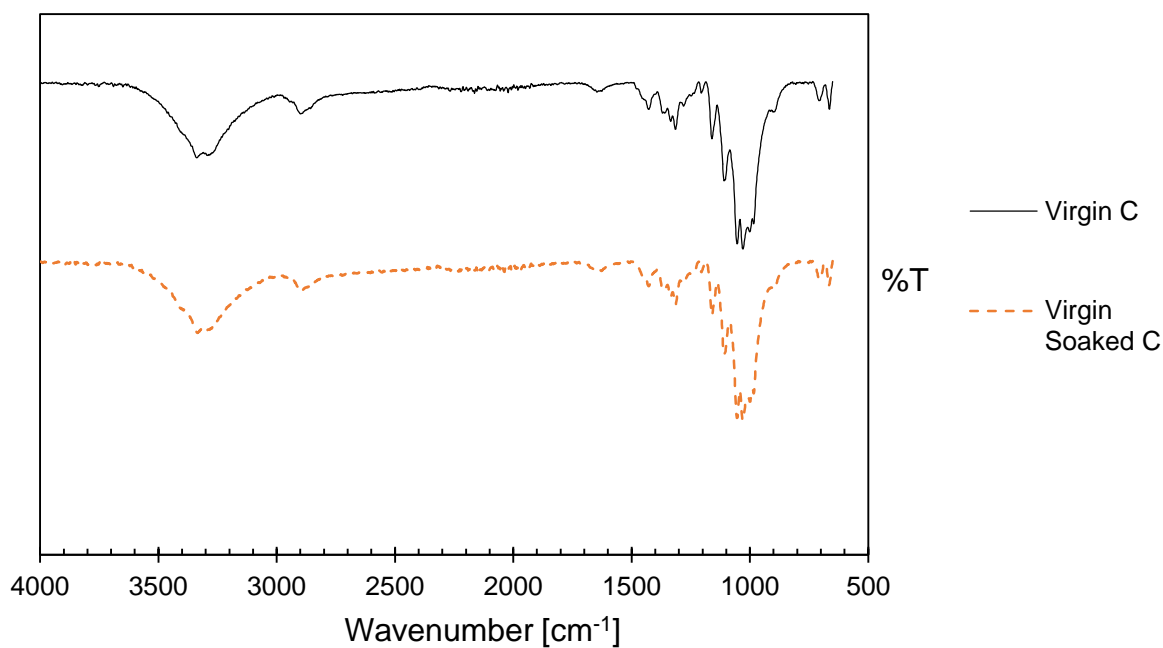


Figure 5.27. FTIR of virgin cotton soaked in at water at 40 °C.

5.2.3. Effect of surfactant concentration at 20 °C

Mass, colour and resistance measurements

Figure 5.28 shows removal as quantified by mass, colour and resistance soaked in various wash solutions at 20 °C. The mass of fabrics that have been soaked in water or surfactant solution at 0.1 times the CMC have actually increased in mass, although the increase is very small. This could in part be due to errors, and may be due to absorption of some water by the cotton or the sebum from the wash solution during soaking. On all measures it can be seen that using twice the CMC of the surfactant in the wash solution gives a small but significant cleaning benefit.

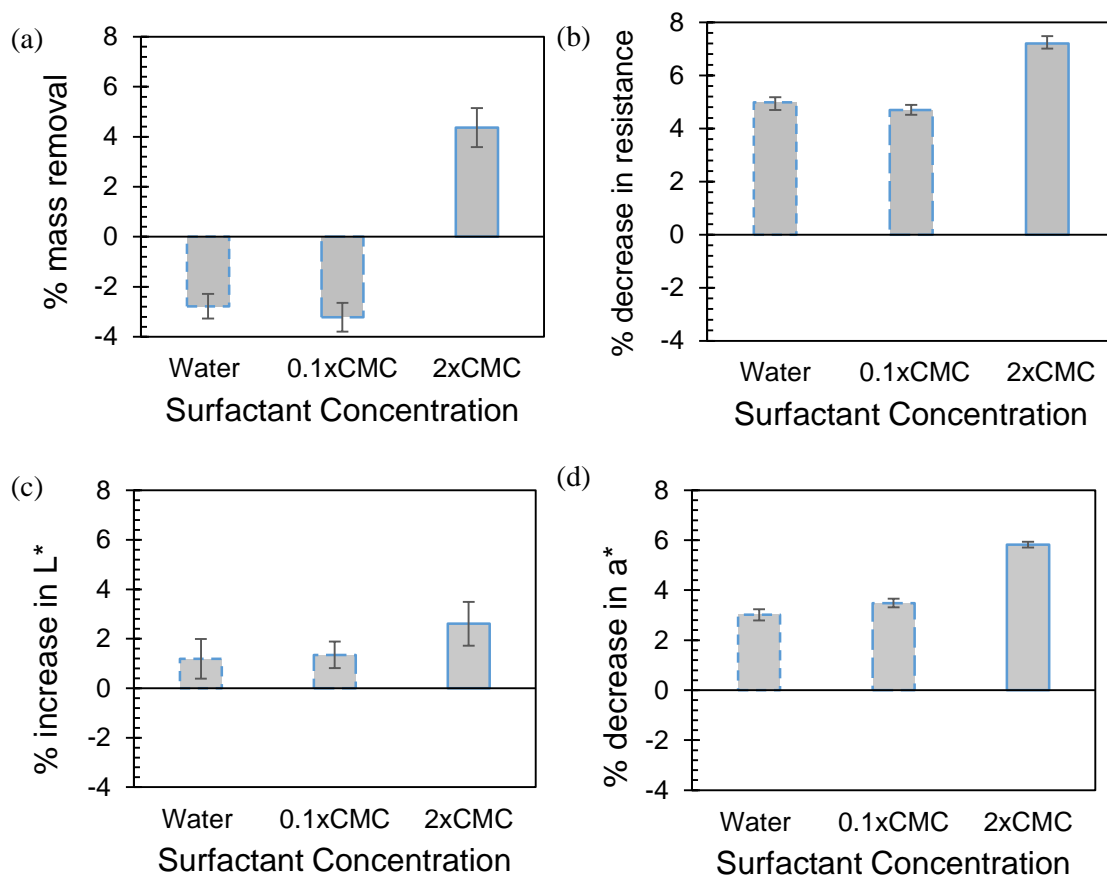


Figure 5.28. Effect of surfactant concentration on chemical action for cotton soiled with sebum at 20 °C. Cleaning is measured by (a) % mass removal, (b) % decrease in resistance, (c) % increase in L^* and (d) % decrease in a^* . The error bars represent \pm one standard deviation for three fabrics. Five measurements were taken from each fabric for colour and resistance.

Colour of top and underside of fabric

It can be seen in Figure 5.29 that removal from the topside and underside is similar for all three wash solutions. The changes are relatively small, which makes the error bars appear larger, although on this scale the differences would not be noticeable.

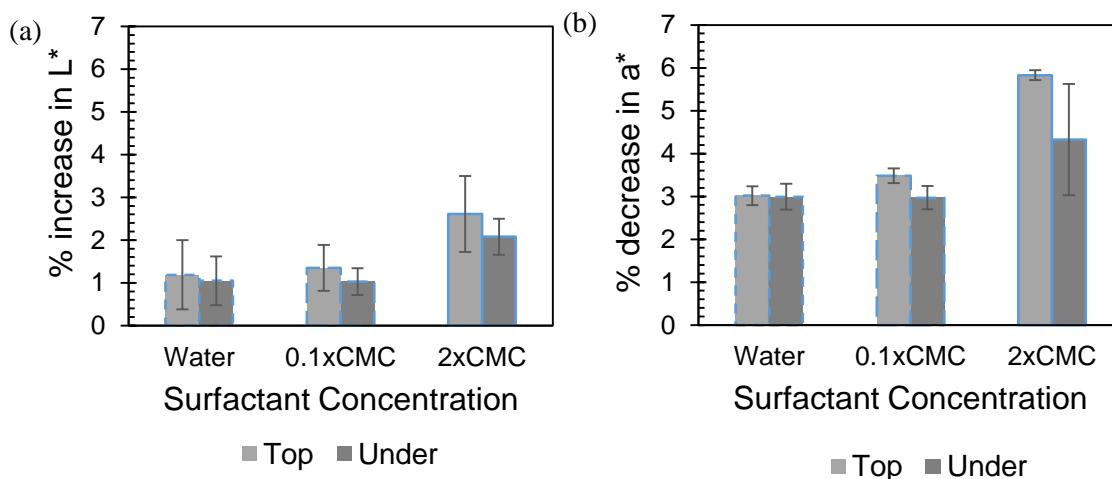


Figure 5.29. Comparison of the colour of the top and underside of cotton soiled with sebum cleaned using chemical action at 20 °C with water and surfactant at a concentration of 0.1 x and 2 x CMC. Colour is measured as (a) L* and (b) a*. The error bars represent \pm one standard deviation for three fabrics. Five measurements were taken from each fabric.

Mass per unit area

Figure 5.30 shows the mass per unit area measurements of the three different soaking conditions. All three fabrics have very similar profiles to the soiled cotton, which is as expected since mass removal overall is low. The sebum does not appear to spread outwards from the central soiled strip to the surrounding clean fabric.

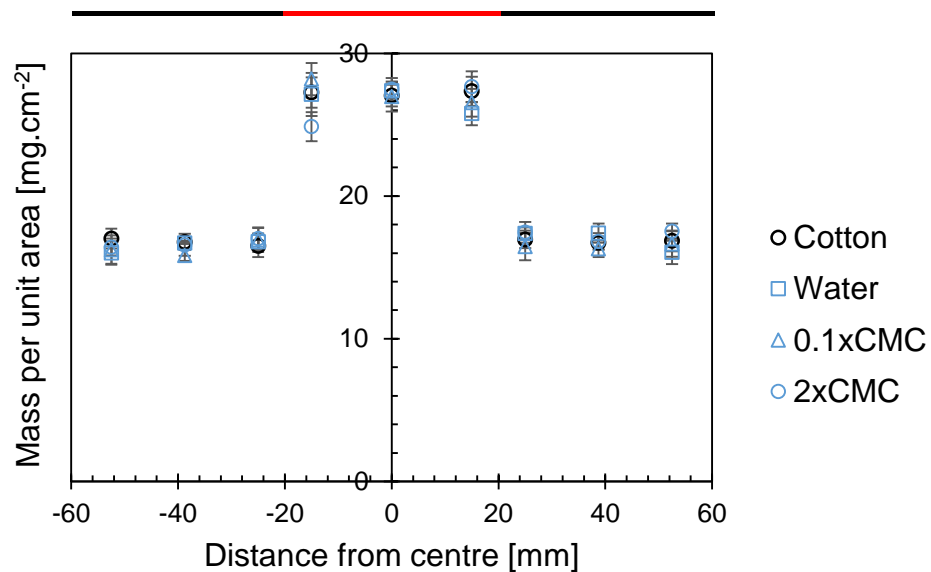


Figure 5.30. Mass per unit area of cotton soiled with sebum cleaned using chemical action at 20 °C with water and surfactant at a concentration of 0.1 x and 2 x CMC. The error bars represent \pm one standard deviation for three fabrics.

FTIR

The FTIR traces, shown in Figure 5.31, show that both the topside and underside of the fabric have the same chemical makeup as the soiled cotton. The same sebum peaks can be observed in these spectra, and there is some masking of the cotton peaks.

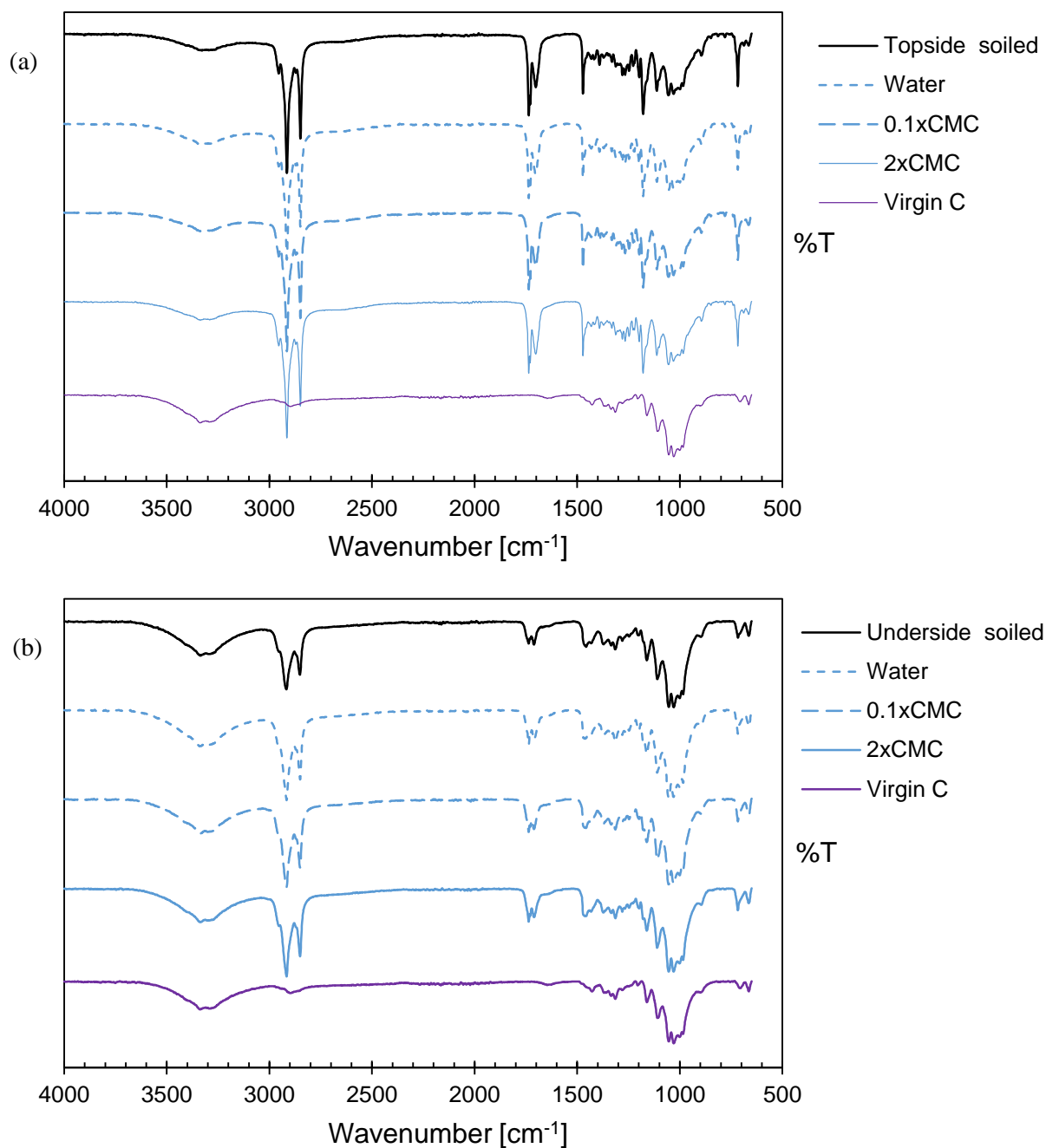


Figure 5.31. FTIR of cotton soiled with sebum cleaned using chemical action at 40 °C with water and surfactant at a concentration of 0.1 x and 2 x CMC. This is compared to soiled and virgin fabrics for both the (a) top and (b) underside of the fabric.

SEM

Figure 5.32 shows SEM images for soaked cotton, which show similarities to soiled cotton. The image at x20 and x100 don't show sebum clearly. At x500, x1000 and x5000 the granular soil can be seen within the yarn, in between individual fibres, and on the fibres.

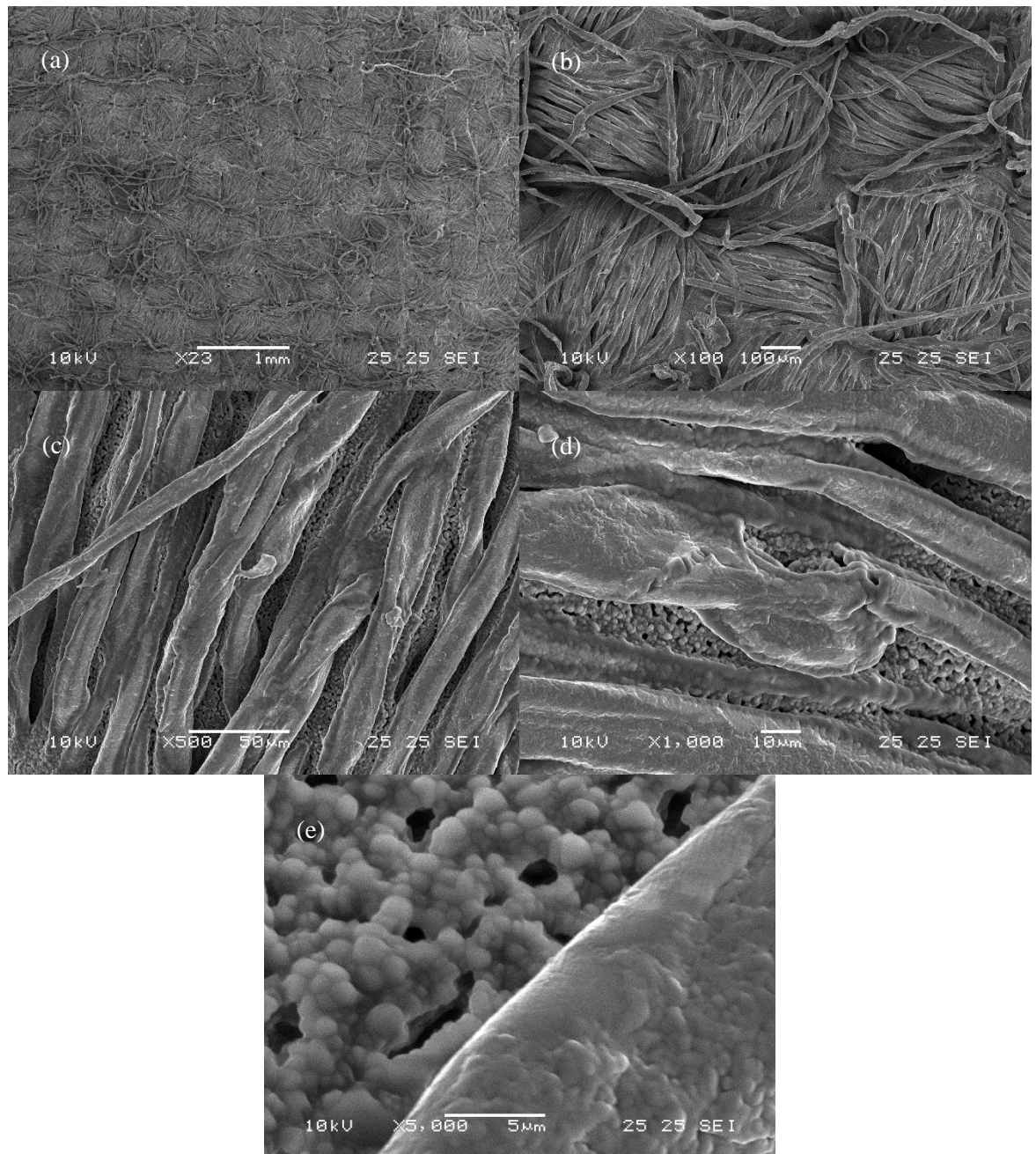


Figure 5.32. SEM images of soiled cotton soaked in 20 °C 2 x CMC surfactant solution at (a) x20 (b) x100 (c) x500 (d) x1000 and (e) x5000 magnifications.

5.3. Discussion on soaking

As expected, when fabrics are soaked, increased removal is found at higher temperatures and when surfactant concentrations above the CMC are used. Increased temperature leads to greater removal

as the sebum will be more liquefied and therefore more accessible to the surfactant in the wash solution, supported by DSC data for the sebum. Increased surfactant concentration, particularly at concentrations above the CMC, aids removal through various mechanisms including roll up and emulsification. For all samples FTIR spectra are similar to soiled fabrics suggesting overall removal is low, which is in line with mass removal data.

For polyester, removal of sebum is approximately linear for all measures of cleaning as temperature is increased, suggesting the benefit seen from using higher temperatures is incremental. This is not the case for cotton, where a small increase is seen when temperature is increased from 20 °C to 40 °C, but a much larger increase in cleaning is observed with 60 °C is used. When cotton is placed in the 60 °C surfactant solution the sebum almost immediately lifts off the surface of the fabric, and collects at the water-air interface. This is not observed with polyester. This may be due to the fact that polyester contains a much thicker layer of soil than the cotton, and the warm water takes longer to penetrate this layer. Also, on polyester, the sebum is much more embedded into the pores of the fabric whereas the soil on cotton sits on the surface so is more accessible.

For both fabrics soaked at 20 °C and 40 °C with different surfactant concentrations the increase in removal of sebum is not linear. Removal with water and 0.1 times the CMC of the surfactant are very similar, suggesting low levels of surfactant offer no additional benefit over water alone. There is a significant increase when twice the CMC of the surfactant is used. It is clear that mechanisms of cleaning that only occur above the CMC, including solubilisation, are very important for cleaning when fabrics are soaked, whereas other mechanisms that can occur below the CMC, such as roll up, are not present when fabrics are soaked.

For polyester, colour loss is less than mass or resistance change, which may be due to some dye remaining on the fabric when sebum has been removed. Resistance change is less than mass change, which may be due to transfer of molten sebum from the surface into the pores of the fabric. This is supported by the fact that the when surfactant solution is used at 60 °C the change in colour of the

underside of the fabric is less than the topside. On polyester, sebum is removed from the central soiled area, and also spreads into the adjacent clean area. This spreading effect is observed more at higher temperatures, explained by the fact that the sebum is more mobile. Cotton, on the other hand, shows higher decrease in resistance than mass or colour change indicating that the sebum has been removed from the pores. This is likely to be because the pores did not contain much sebum initially. Mass per unit area results also do not show spreading of sebum to the unsoiled area of the fabric, suggesting the sebum is less mobile on the surface of the fabric.

Chapter 6: Effect of Hydrodynamics

In this chapter the effect of hydrodynamics on fabric cleaning are studied over a range of temperatures and surfactant concentrations. This includes the effect of flow across and through the fabric as well as use of Fluid Dynamic Gauging to investigate the strength of adhesion of soil to the surface.

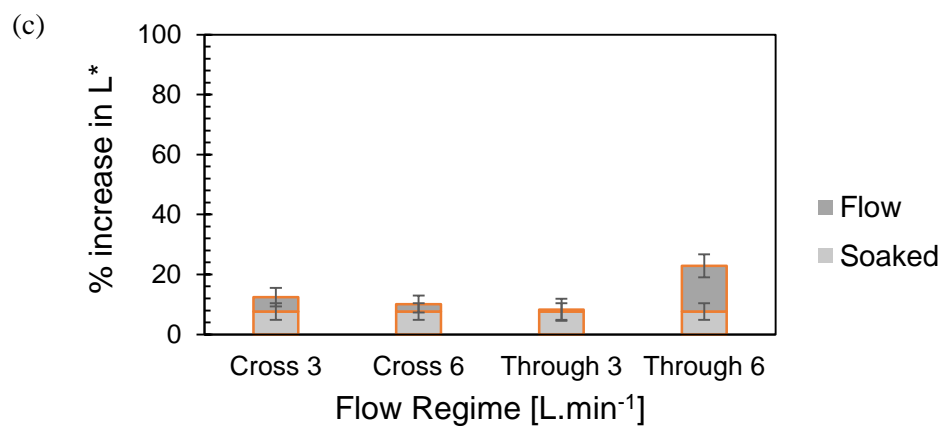
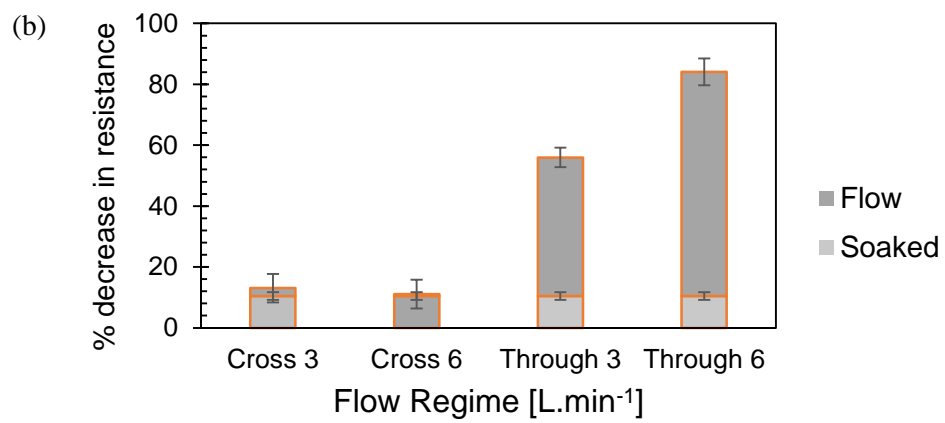
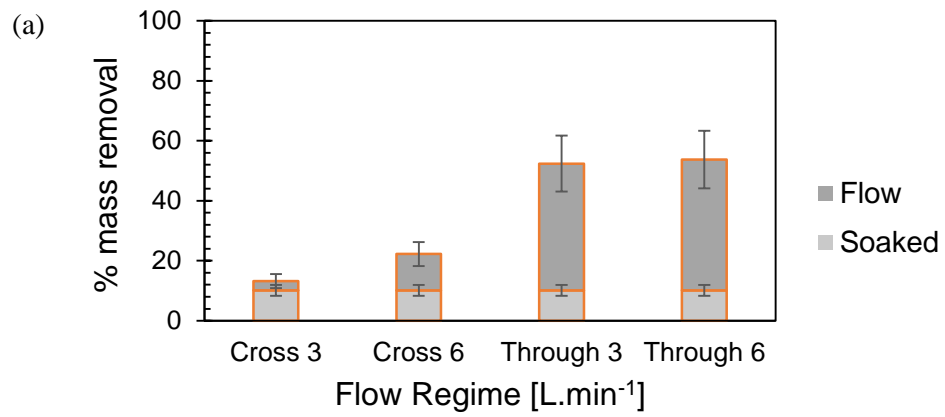
6.1. Flow rig

6.1.1. Polyester

6.1.1.1. Establishing flow conditions

Mass, colour and resistance measurements

Figure 6.1 shows removal for different flow regimes, cross and through flow, and different flow rates, 3 L.min⁻¹ and 6 L.min⁻¹, at 40 °C with twice the CMC of the surfactant. These results enable establishment the combination of flow conditions that will lead to the greatest removal, and as such will be used for all future experiments. For all four measures of cleaning - mass, lightness, redness and resistance to flow of water - removal is highest for through flow at 6 L.min⁻¹. Through flow increases removal of sebum as you increase the flow rate. This is because as you increase the flow of water through the fabric, more sebum will be removed from the pores. This is evidenced by the fact that the decrease in resistance is much higher for through flow. Counterintuitively, cleaning is decreased by increasing the flow rate when cross flow is used. It is suspected that the higher shear stress imparted on the fabric by the flow of water across the surface forces some of the sebum into the pores of the fabric. Again, this is confirmed by resistance results, which show little improvement after cross flow experiments at 3 L.min⁻¹ when compared to fabric soaked in surfactant solution of the same temperature and concentration. For cross flow at 6 L.min⁻¹ resistance is actually found to be less than the soaked fabric.



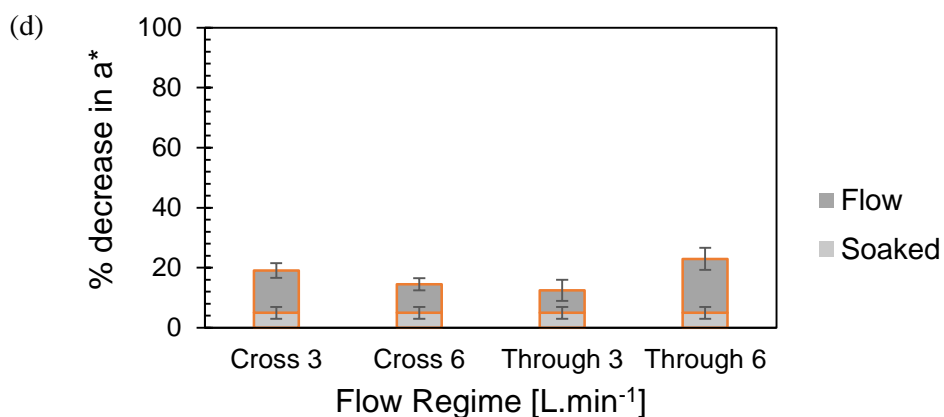
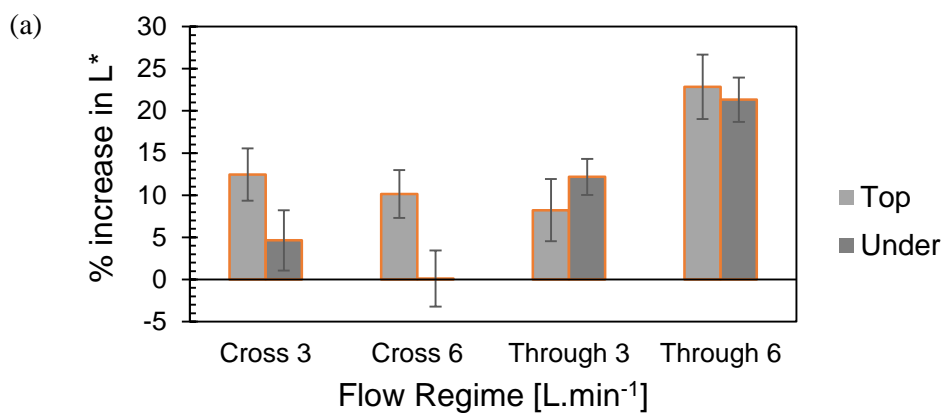


Figure 6.1. Comparison of flow regimes for polyester soiled with sebum cleaned using the flow rig at 40 °C with surfactant at a concentration of 2 x CMC. Four flow regimes were used comprising of cross and through flow, and 3 and 6 L.min⁻¹. Cleaning is measured by (a) % mass removal, (b) % decrease in resistance, (c) % increase in L* and (d) % decrease in a*. The error bars represent \pm one standard deviation for three fabrics. Five measurements were taken from each fabric.

Colour of top and underside of fabric

When the colour of the topside and underside of the fabric are considered, Figure 6.2 shows that removal on both sides for through flow is fairly similar. On the other hand, removal on the underside of fabrics cleaned with cross flow show significantly less removal than the topside of the fabric. It is suspected that some removal is seen due to the temperature of water and surfactant solution, which will sit in the bottom of the flow chamber during the flow experiment and give an effect similar to that of soaking. However it is clear that without flow through the fabric, removal from the underside is very low.



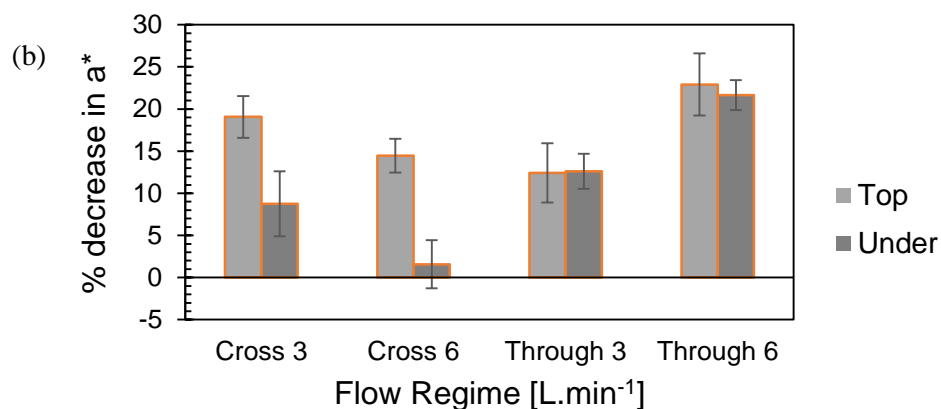
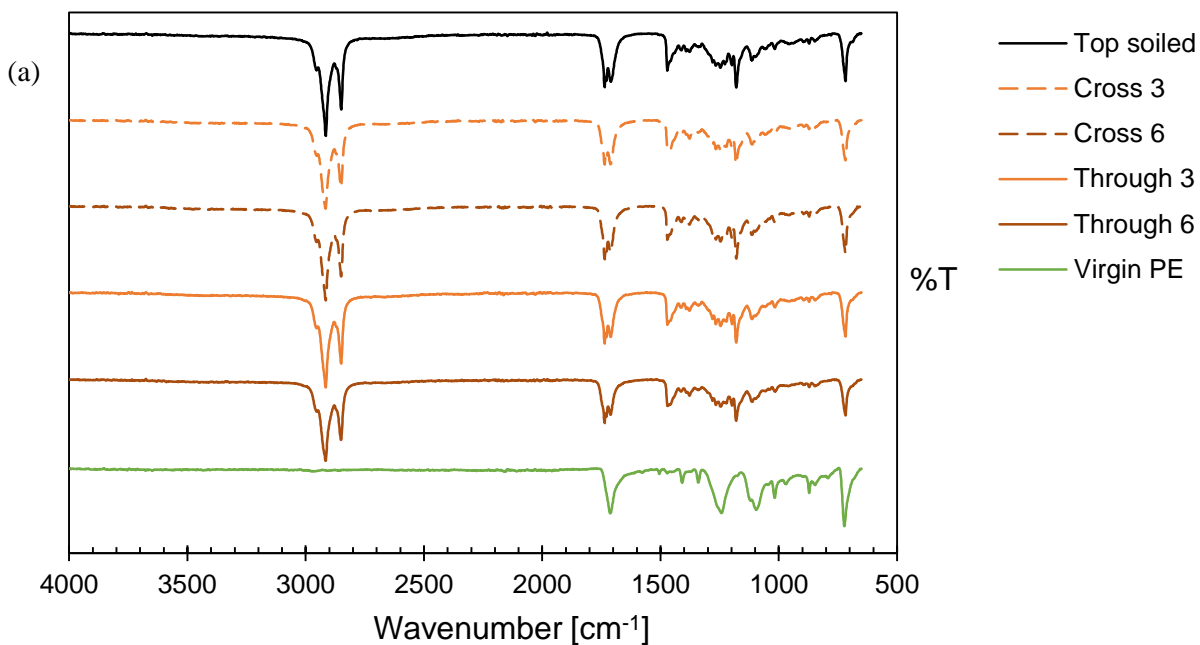


Figure 6.2. Comparison of the colour of the top and underside of polyester soiled with sebum cleaned using the flow rig at 40 °C with surfactant at a concentration of 2 x CMC. Four flow regimes were used comprising of cross and through flow, and 3 and 6 L.min⁻¹. Colour is measured as (a) L* and (b) a*. The error bars represent \pm one standard deviation for three fabrics. Five measurements were taken from each fabric.

FTIR

Figure 6.3 shows the FTIR spectra of the topside and underside of polyester subject to cleaning using the different flow regimes. It can be seen that the spectra of these fabrics are very similar to the soiled polyester trace, which is to be expected since only about 25 % of the mass of sebum has been removed on the most cleaned sample.



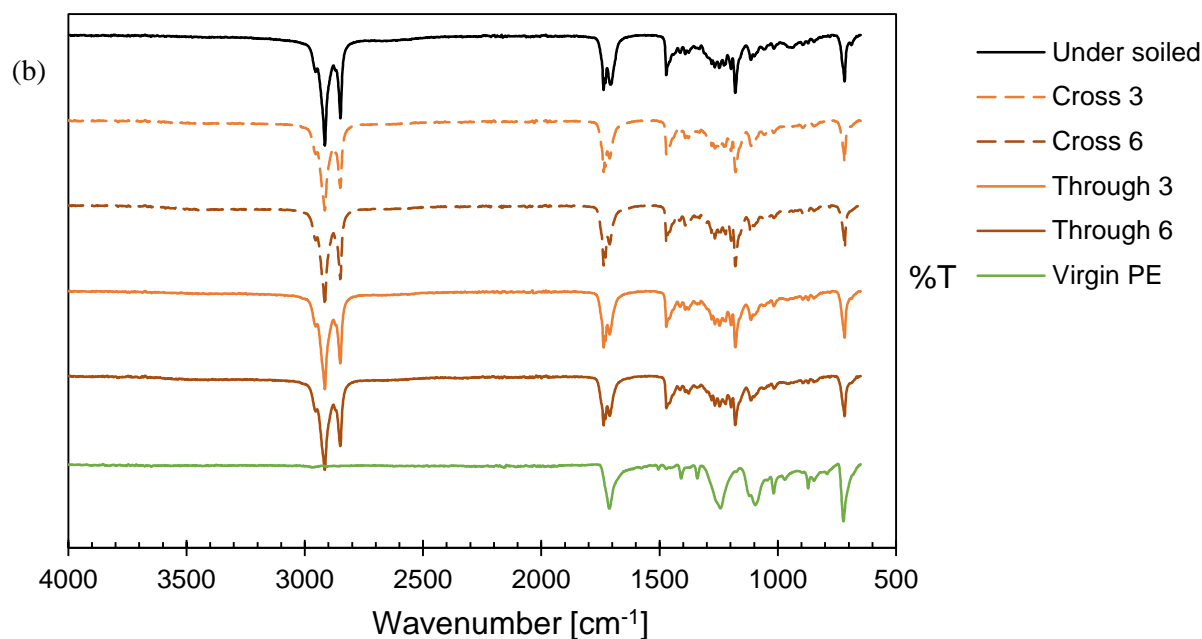


Figure 6.3. FTIR of polyester soiled with sebum cleaned using the flow rig at 40 °C with surfactant at a concentration of 2 x CMC. Four flow regimes were used comprising of cross and through flow, and 3 L.min⁻¹ and 6 L.min⁻¹. This is compared to soiled and virgin polyester for both the (a) top and (b) underside of the fabric.

Flow conditions

It was decided that 6 L.min⁻¹ through flow would be used in further testing with the flow rig as this caused the greatest removal of sebum when all measures of cleanliness were evaluated.

6.1.1.2. Effect of Temperature

Mass, colour and resistance measurements

Figure 6.4 shows that, for all measures of cleaning, increased temperature leads to increased removal of sebum. For mass and colour the increase when flow is used compared to soaking alone is much greater for 60 °C than the lower temperatures. However, for resistance, the decrease caused by flow of water compared to soaking alone is very similar for all three temperatures. This suggests that the force of flow of water is responsible for cleaning within the pores, pushing the sebum through the fabric and away in the wash solution. In contrast, the higher temperatures may aid removal of molten sebum from the surface of the fabric leading to overall higher mass and colour loss.

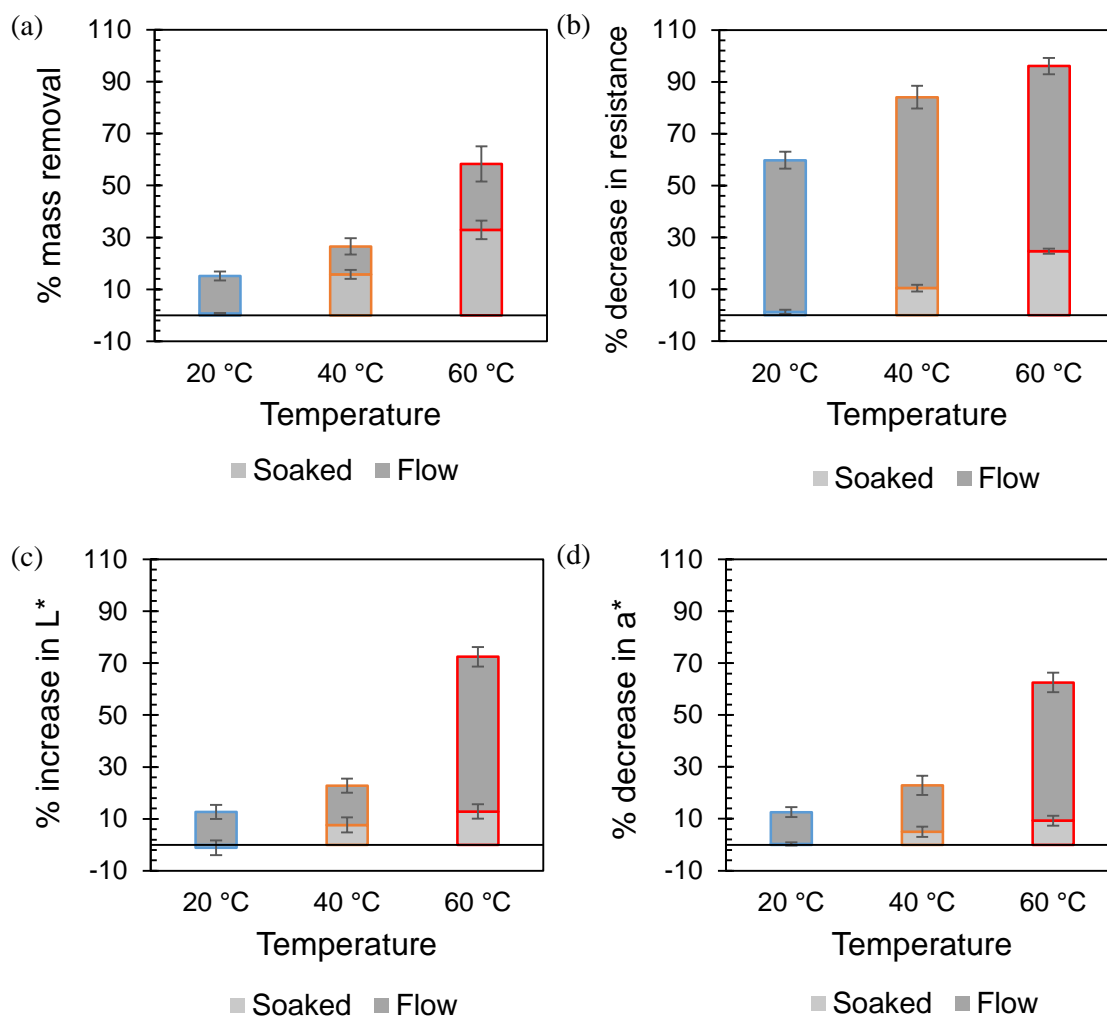


Figure 6.4. Effect of temperature on cleaning by the flow rig for polyester soiled with sebum. Surfactant was used at a concentration of 2 x CMC. Cleaning is measured by (a) % mass removal, (b) % decrease in resistance, (c) % increase in L^* and (d) % decrease in a^* . The error bars represent \pm one standard deviation for three fabrics. Five measurements were taken from each fabric for colour and resistance.

Colour of top and underside of fabric

Figure 6.5 shows the colour of the top and underside of the fabric. Removal from the top and underside is quite similar, however for all temperatures the topside shows slightly higher removal of sebum, which may be because the wash solution passes over this surface to get to the pores and causes some removal.

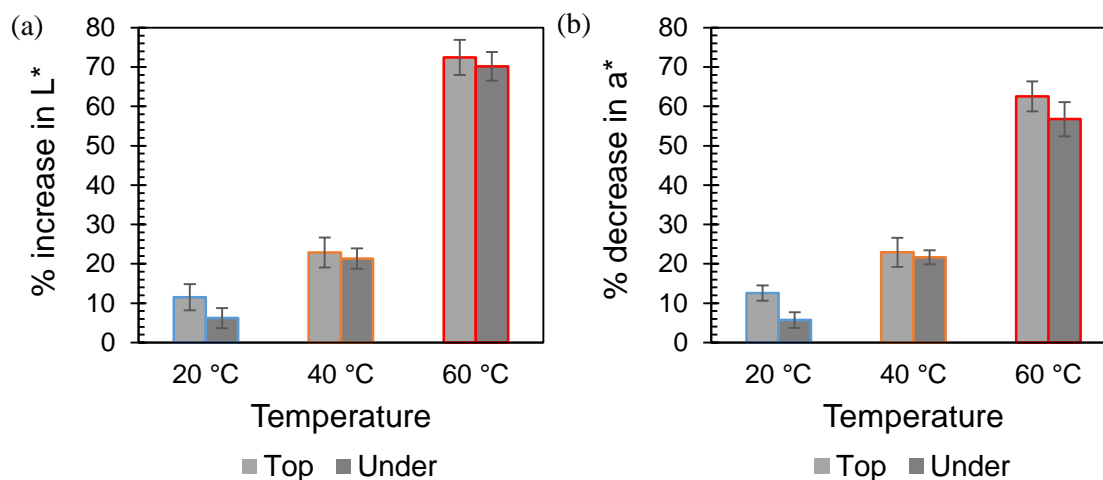


Figure 6.5. Comparison of the colour of the top and underside of polyester soiled with sebum cleaned using the flow rig at 20 °C, 40 °C and 60 °C with surfactant at a concentration of 2 x CMC. Colour is measured as (a) L^* and (b) a^* . The error bars represent \pm one standard deviation for three fabrics. Five measurements were taken from each fabric.

Mass per unit area

Since the flow channel is only the middle 1 cm of the soiled area the fabrics would be expected to have a much lower mass per unit area in the centre, with less removal outside of the flow area. This is what we see on Figure 6.6. At 60 °C the mass of the central area is almost equal to that of virgin polyester. The two surrounding soiled areas also show significant removal, which is likely to be caused by some wash solution at the higher temperature seeping into this area and liquefying the sebum. The central area of the samples washed at the two lower temperatures also shows higher removal, but significantly less than is seen at 60 °C. There is no removal in the adjacent area on the soiled strip, confirming that it is the high temperature that causes removal on the fabric washed at 60 °C. Some increase in mass is seen in the area adjacent to the soiled strip for 60 °C. This may be due to the spreading of molten sebum, and would explain a proportion of the mass loss from the adjacent soiled area.

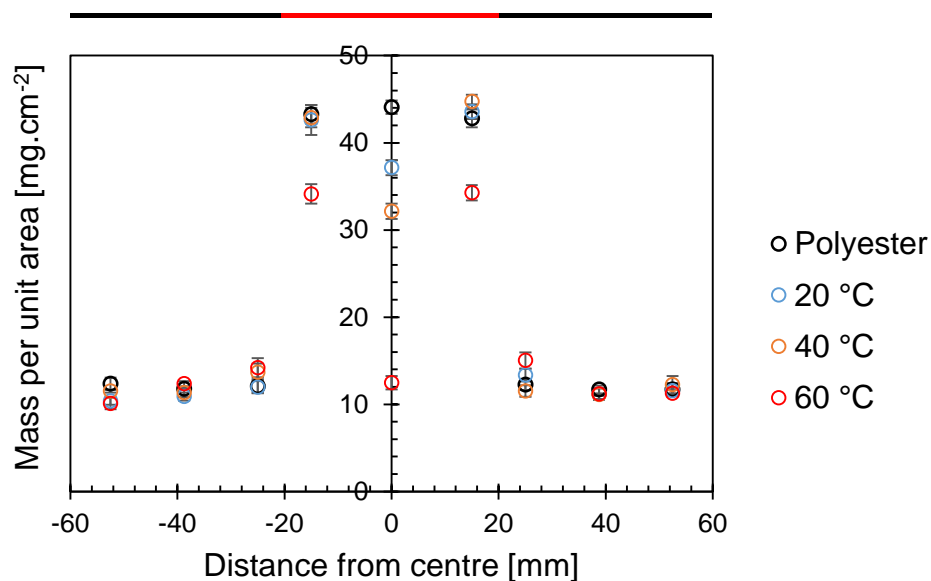


Figure 6.6. Mass per unit area of polyester soiled with sebum cleaned using the flow rig at 20 °C, 40 °C and 60 °C with surfactant at a concentration of 2 x CMC. The error bars represent \pm one standard deviation for three fabrics.

FTIR

Figure 6.7 shows the FTIR spectra of the top and under side of the fabrics washed at various temperatures compared to virgin and soiled polyester. It can be seen that fabrics washed at 20 °C and 40 °C are very similar to soiled polyester and show the characteristic sebum peaks, for example at 2920 and 2850 cm^{-1} . On the other hand, fabrics washed at 60 °C only show very shallow sebum peaks, and some polyester peaks that had been masked by the sebum are now visible, such as the peaks at 1708 and 1240 cm^{-1} . This is in line with mass removal results.

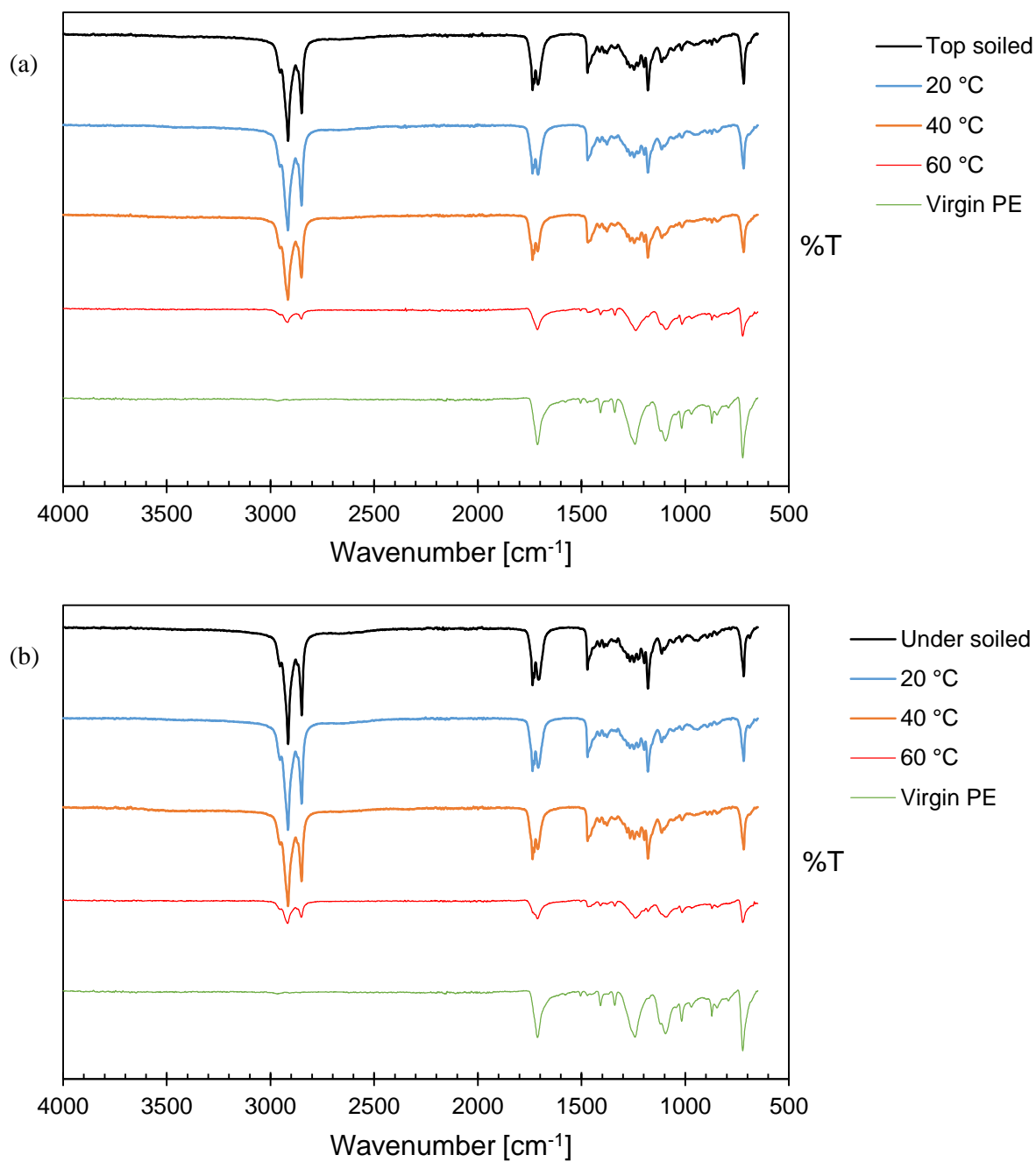
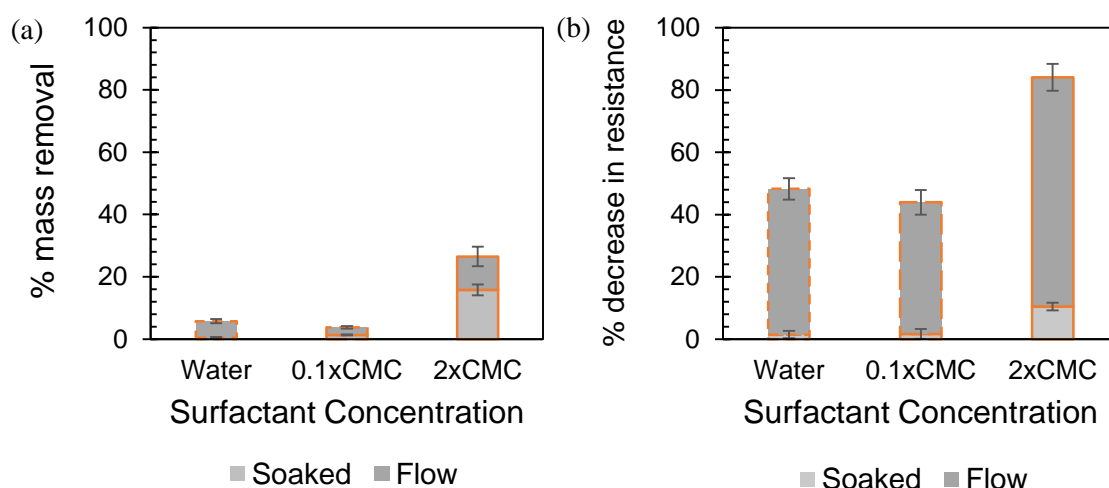


Figure 6.7. FTIR of polyester soiled with sebum cleaned using the flow rig at 20 °C, 40 °C and 60 °C with surfactant at a concentration of 2 x CMC. This is compared to soiled and virgin polyester for both the (a) top and (b) underside of the fabric.

6.1.1.3. Effect of surfactant concentration at 40 °C

Mass, colour and resistance measurements

The mass change, colour change and resistance change are presented in Figure 6.8. It can be seen that removal is much higher with wash solution containing surfactant at twice its CMC suggesting there is a synergistic cleaning effect. A synergistic effect indicates that two or more actions combine to produce an effect greater than the sum of their individual effects, in this case the coupling of flow with surfactant. Cleaning using flow with water and 0.1 times the CMC of the surfactant offer very little cleaning benefit when cleaning is judged by mass and colour removal. However, a significant benefit is seen when resistance is considered. This is to be expected as through flow forces wash solution through the pores, which will remove sebum that has deposited there.



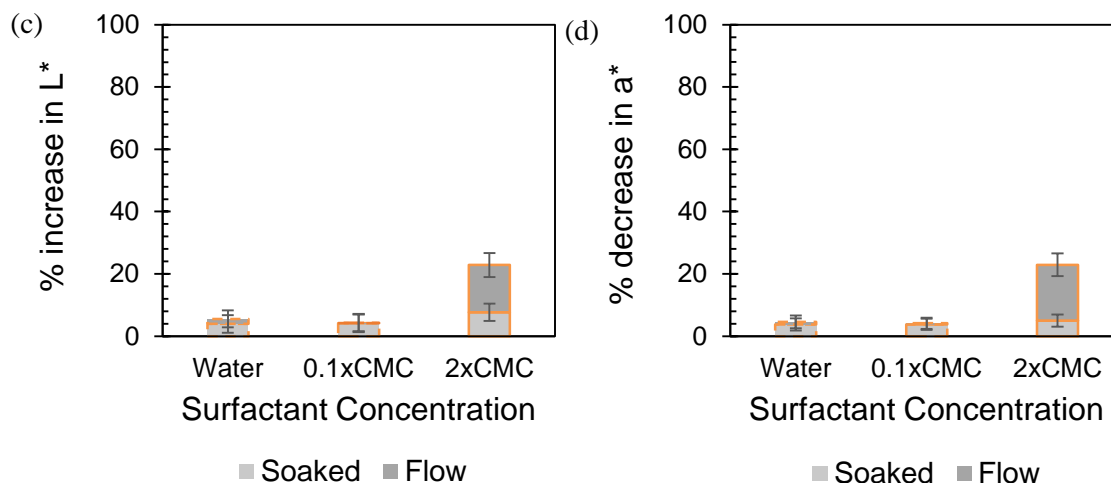


Figure 6.8. Effect of surfactant concentration on cleaning by the flow rig at 40 °C for polyester soiled with sebum. Cleaning is measured by (a) % mass removal, (b) % decrease in resistance, (c) % increase in L^* and (d) % decrease in a^* . The error bars represent \pm one standard deviation for three fabrics. Five measurements were taken from each fabric for colour and resistance.

Colour of top and underside of fabric

The colour of the underside of the fabric is dirtier than the soiled fabric for water and 0.1 times the CMC of the surfactant, as shown in Figure 6.9. This suggests sebum is removed from the top surface of the fabric and pulled through the fabric, then deposits on the underside of the fabric rather than being carried away in the wash solution. When twice the CMC is used it is thought that the surfactant plays a role in suspending the soil in the wash solution, which explains why removal from the top and underside are approximately the same under this condition.

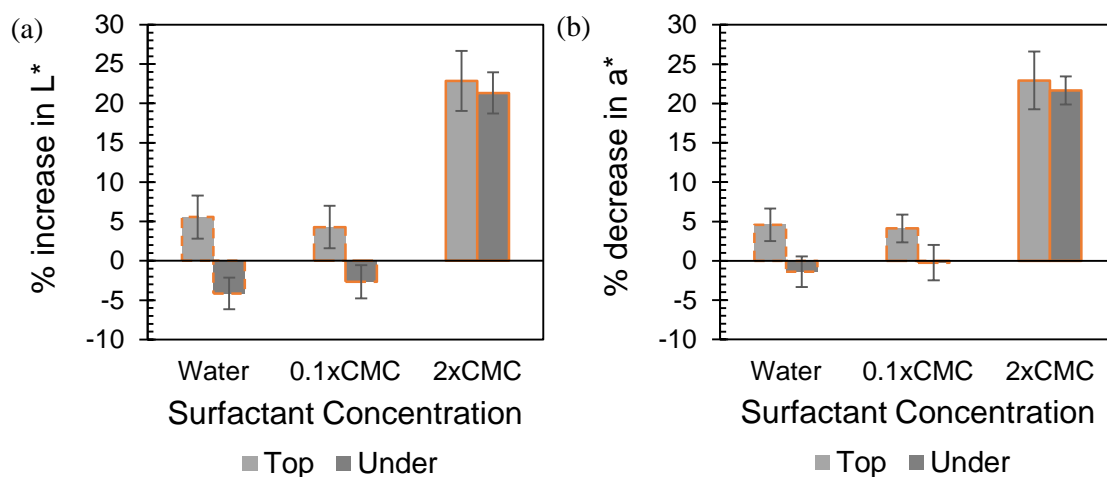


Figure 6.9. Comparison of the colour of the top and underside of polyester soiled with sebum cleaned using the flow rig at 40 °C with water and surfactant at a concentration of 0.1 x and 2 x CMC. Colour is measured as (a) L* and (b) a*. The error bars represent \pm one standard deviation for three fabrics. Five measurements were taken from each fabric.

Mass per unit area

Figure 6.10 shows that, at 40 °C, mass loss is from the central line of the soiled area, which is where flow is directed. Mass loss when twice the CMC of the surfactant is used is much more than for water or 0.1 times the CMC of the surfactant, indicating that at low concentrations the surfactant does not offer a benefit over water alone when flow is considered. This also supports the mechanism suggested previously that surfactant aids removal by suspending the sebum in the wash solution.

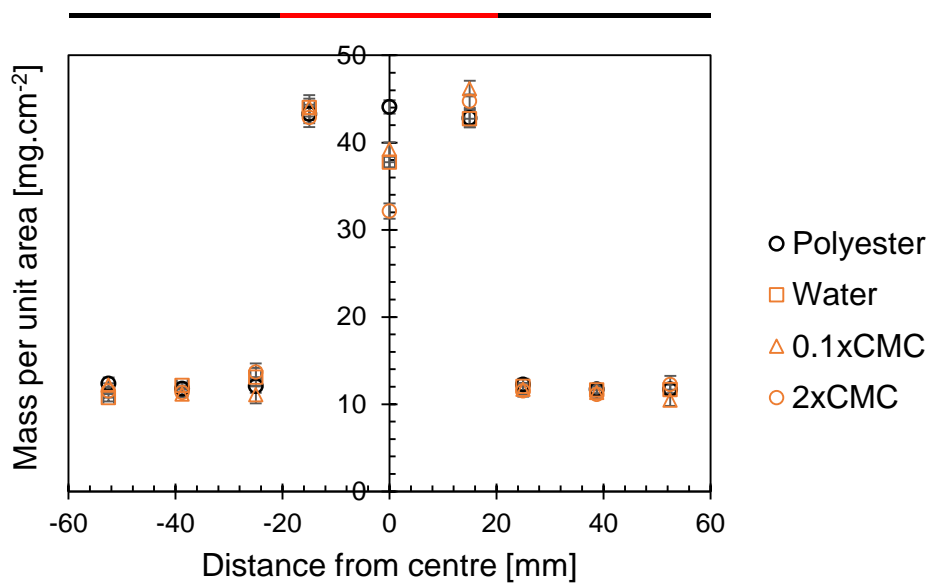


Figure 6.10. Mass per unit area of polyester soiled with sebum cleaned using the flow rig at 40 °C with water and surfactant at a concentration of 0.1 x and 2 x CMC. The error bars represent \pm one standard deviation for three fabrics.

FTIR

FTIR spectra, presented in Figure 6.11, show very few differences between the three wash solutions and soiled polyester. This suggests that the chemical make up of the surface is still very similar to the soiled polyester after flow experiments.

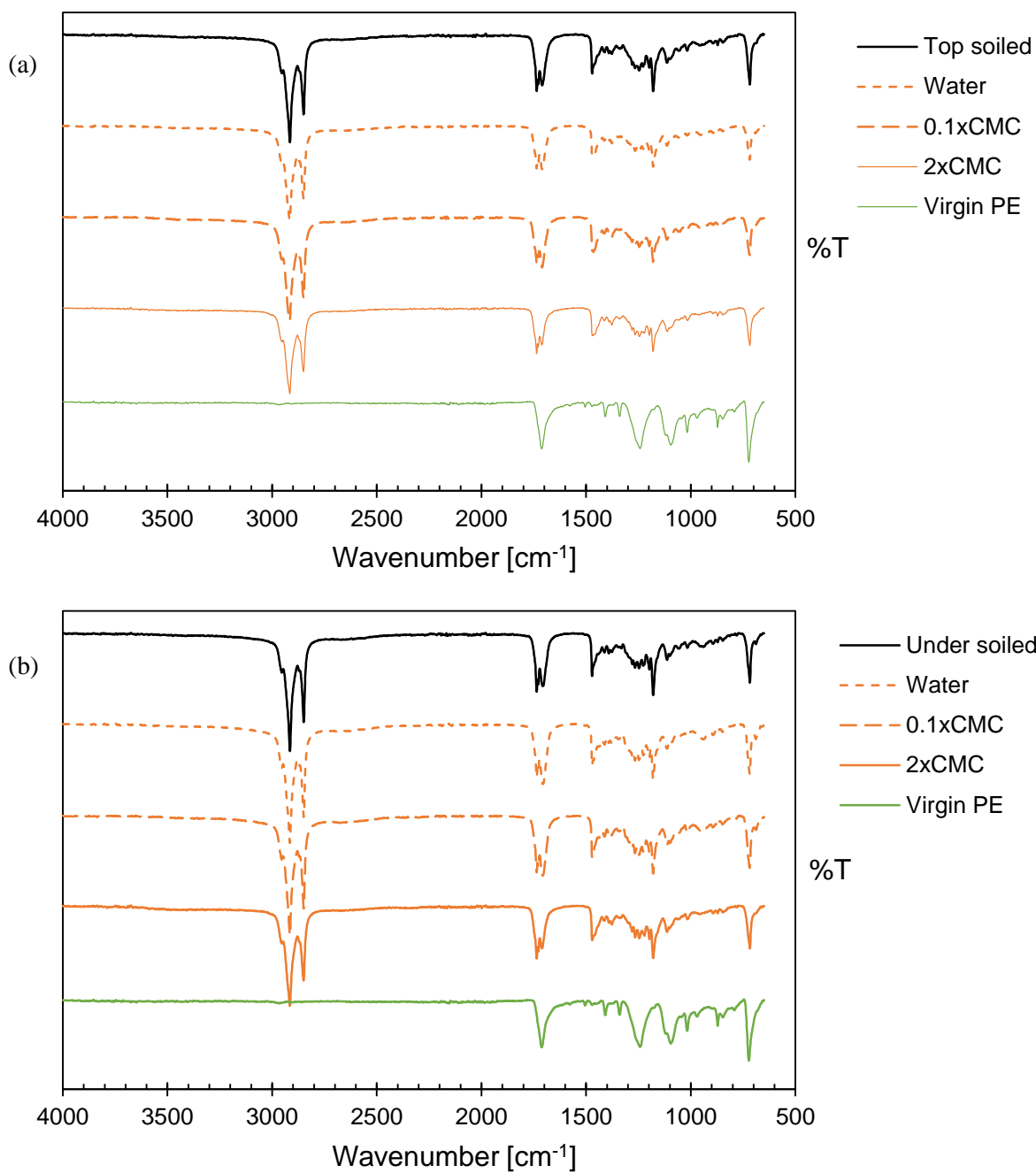


Figure 6.11. FTIR of polyester soiled with sebum cleaned using the flow rig at 40 °C with water and surfactant at a concentration of 0.1 x and 2 x CMC. This is compared to soiled and virgin polyester for both the (a) top and (b) underside of the fabric.

6.1.1.4. Effect of surfactant concentration at 20 °C

Mass, colour and resistance measurements

When mass change, colour change and resistance change are investigated, as in Figure 6.12, it can be seen that removal is much higher when the surfactant is used at twice the CMC. This is thought to be because the surfactant suspends the sebum in the wash solution aiding removal. On all measures, surfactant at 0.1 times the CMC leads to less sebum removal than water alone, although the difference is very small and is only significant for mass removal.

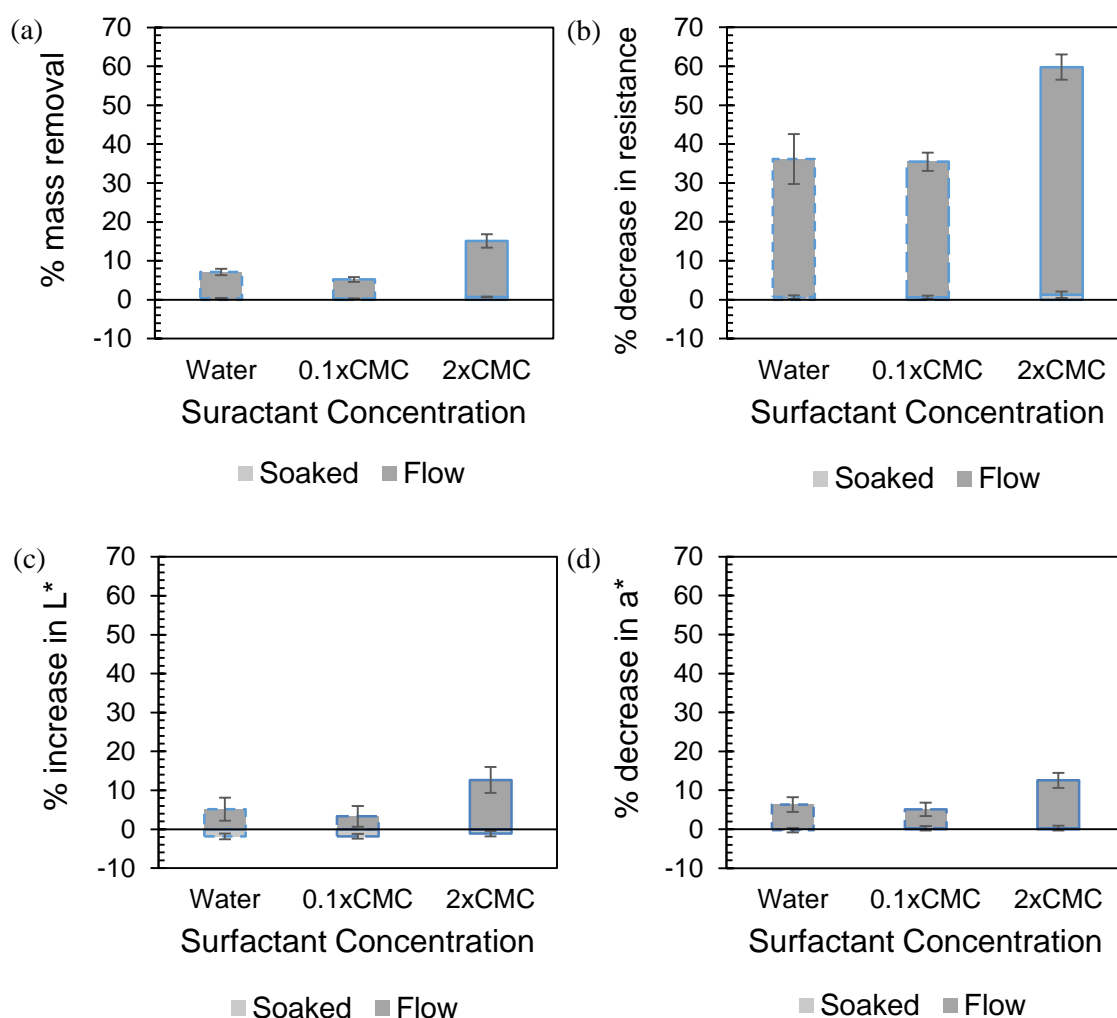


Figure 6.12. Effect of surfactant concentration on cleaning by the flow rig at 20 °C for polyester soiled with sebum. Cleaning is measured by (a) % mass removal, (b) % decrease in resistance, (c) % increase in L* and (d) % decrease in a*. The error bars represent \pm one standard deviation for three fabrics. Five measurements were taken from each fabric for colour and resistance.

Colour of top and underside of fabric

As shown in Figure 6.13, when the colour of the topside and underside are considered significantly more removal from the topside can be seen. In terms of lightness (L^*), the colour is darker on the underside than for soiled polyester. This may be because the flow of wash solution has transported some of the sebum from the top surface as it passes over this area and deposited it on the underside of the fabric.

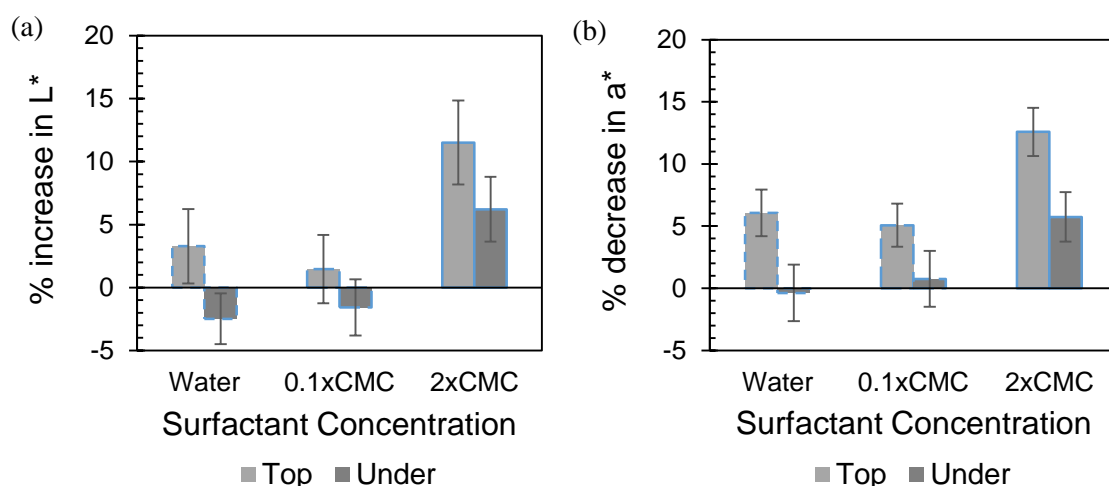


Figure 6.13. Comparison of the colour of the top and underside of polyester soiled with sebum cleaned using the flow rig at 20 °C with water and surfactant at a concentration of 0.1 x and 2 x CMC. Colour is measured as (a) L^* and (b) a^* . The error bars represent \pm one standard deviation for three fabrics. Five measurements were taken from each fabric.

Mass per unit area

Mass per unit area results, presented in Figure 6.14, show that more sebum is removed when twice the CMC of the surfactant is used. A smaller amount of removal is seen when water or 0.1 times the CMC are used. Removal is from the central strip of the soiled area, where the flow of wash solution is directed. It appears that some sebum has been lost from the strip at -15 mm from the centre for 0.1 times the CMC of the surfactant, however the mass is higher for the equivalent strip at +15 mm suggesting the distribution of sebum may not have been equal to begin with. No spreading of sebum to the clean area of the fabric is observed at 20 °C.

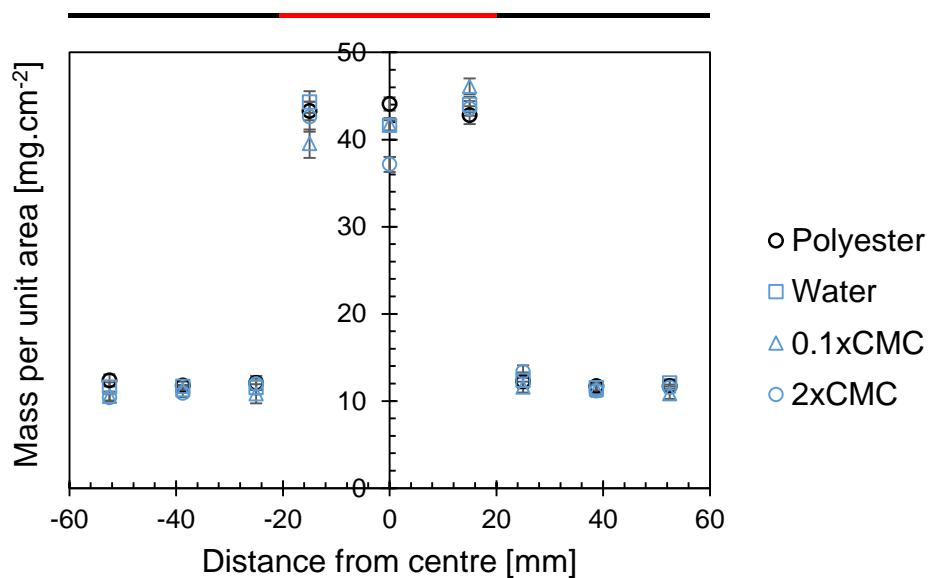


Figure 6.14. Mass per unit area of polyester soiled with sebum cleaned using the flow rig at 20 °C with water and surfactant at a concentration of 0.1 x and 2 x CMC. The error bars represent \pm one standard deviation for three fabrics.

FTIR

Figure 6.15 shows FTIR spectra of fabrics washed using flow at 20 °C. It can be seen that all three surfactant concentrations are very similar to soiled polyester suggesting that cleaning has not removed a significant amount of sebum as the chemical make up of the surface has not changed.

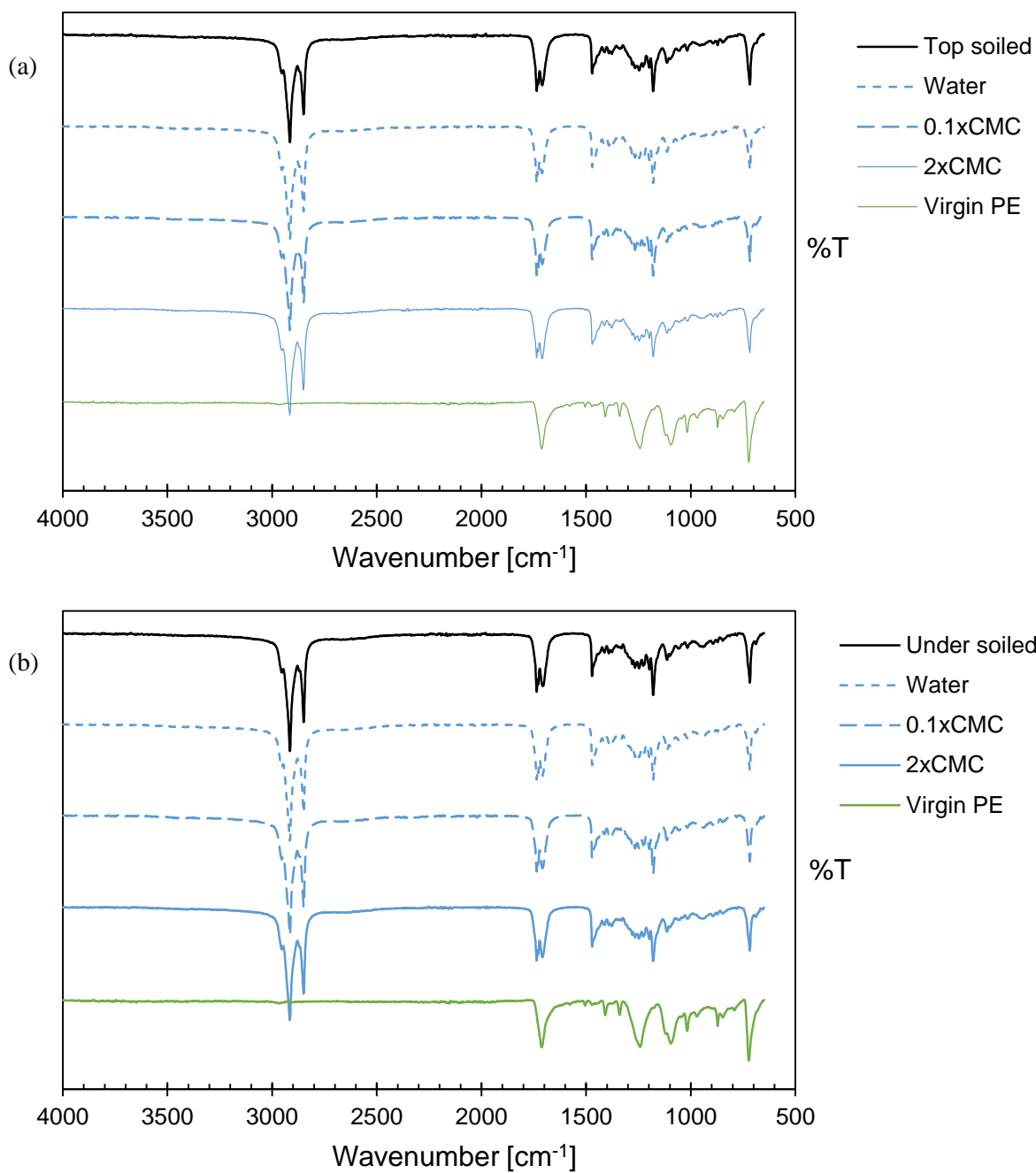


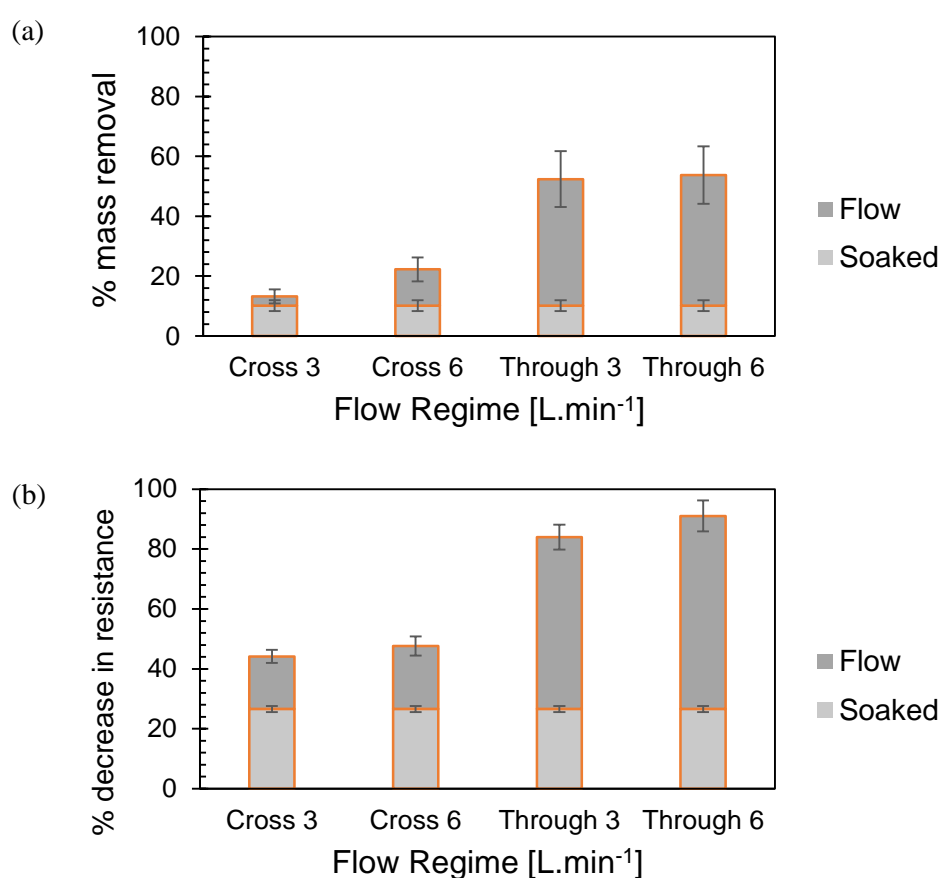
Figure 6.15. FTIR of polyester soiled with sebum cleaned using the flow rig at 20 °C with water and surfactant at a concentration of 0.1 x and 2 x CMC. This is compared to soiled and virgin polyester for both the (a) top and (b) underside of the fabric.

6.1.2. Cotton

6.1.2.1. Establishing flow conditions

Mass, colour and resistance measurement

When a range of flow conditions are tested for cotton, with cleaning judged by mass loss, colour change and resistance change, it can be seen that removal is much higher for through flow compared to cross flow, as shown in Figure 6.16. Again this is likely to be because the force of the water through the pores removes sebum from that area. On all four measures removal is very similar for both flow rates under both cross flow and through flow conditions. This is in contrast to polyester, as shown in Figure 6.1, where flow rate has much more of an effect on cleaning. This suggests that, for cotton, the action of the water causes the cleaning independent of the flow rate under the conditions selected.



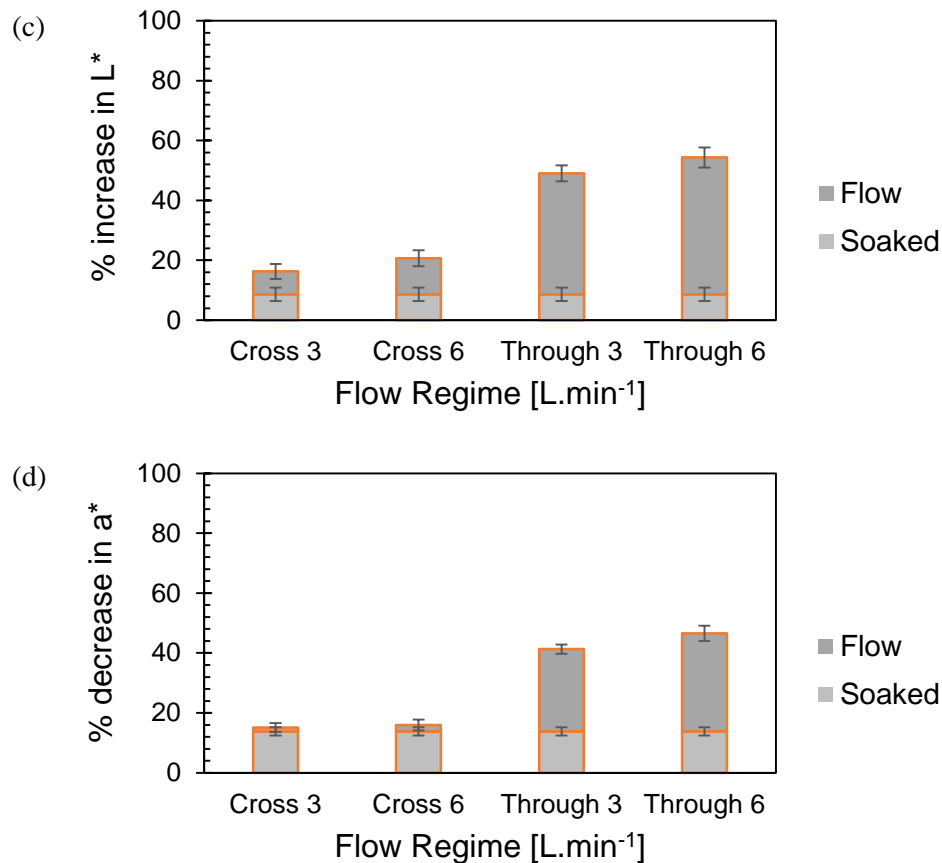


Figure 6.16. Comparison of flow regimes for cotton soiled with sebum cleaned using the flow rig at 40 °C with surfactant at a concentration of 2 x CMC. Four flow regimes were used comprising of cross and through flow, and 3 and 6 L.min⁻¹. Cleaning is measured by (a) % mass removal, (b) % decrease in resistance, (c) % increase in L* and (d) % decrease in a*. The error bars represent ± one standard deviation for three fabrics. Five measurements were taken from each fabric.

Colour of top and underside of fabric

Similar to polyester, the top and underside of fabrics subject to through flow show similar improvement as shown in Figure 6.17. For cross flow a larger change in the colour indicating some cleaning of the topside of the fabric can be observed, whereas the underside of the fabric only shows a small improvement (L*) or is slightly worse than the original soiled fabric (a*). Through flow is thought to remove sebum from the pores of the fabric, but cross flow only cleans the top side, which is the surface the flow passes over.

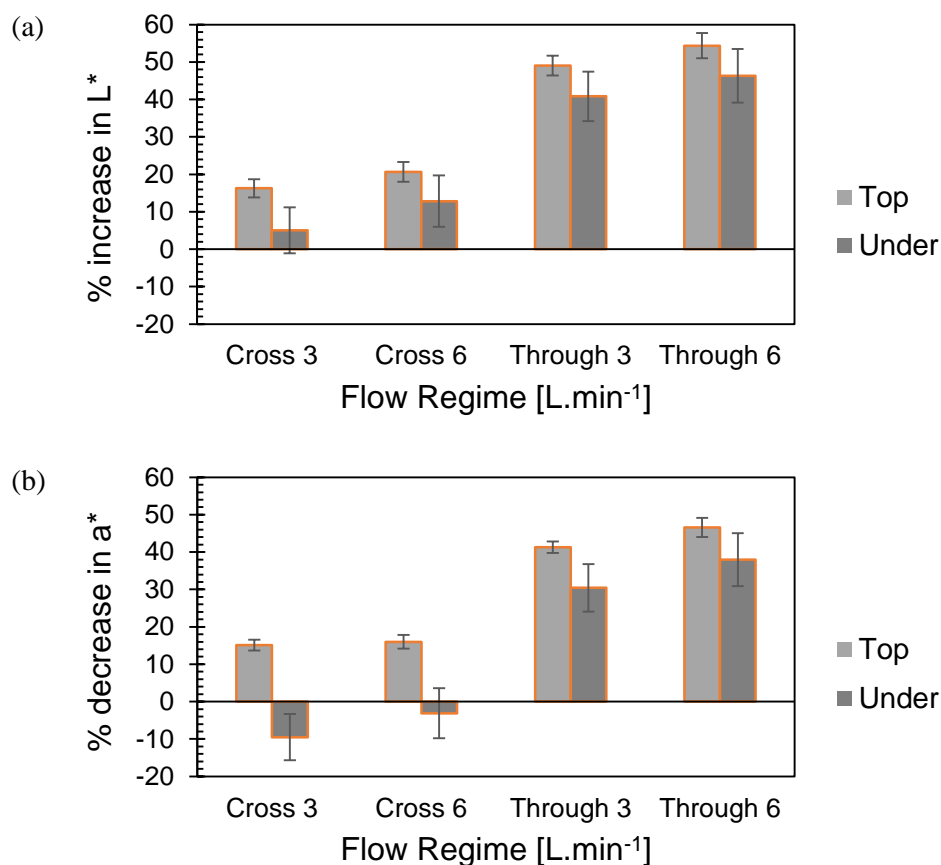


Figure 6.17. Comparison of the colour of the top and underside of cotton soiled with sebum cleaned using the flow rig at 40 °C with surfactant at a concentration of 2 x CMC. Four flow regimes were used comprising of cross and through flow, and 3 and 6 L.min⁻¹. Colour is measured as (a) L* and (b) a*. The error bars represent \pm one standard deviation for three fabrics. Five measurements were taken from each fabric.

FTIR

Figure 6.18 shows the FTIR spectra of the top and underside of the fabrics for the different flow regimes. On the topside of the fabric the distinctive pair of sebum peaks at 2890 and 2830 cm⁻¹ have reduced in size when compared to the original soiled cotton, whereas the same reduction is not seen for cross flow fabrics. On all samples the broad cotton peak around 3310 cm⁻¹ can be observed, and doesn't appear to be to have been masked by the sebum. On the underside of the fabric for through flow fabrics the peaks at 2850 and 2910 cm⁻¹ have significantly reduced indicating removal of sebum from the underside of the fabric. The sebum peaks at 1710 and 1740 cm⁻¹ have also reduced in size, so much so that the former peak is not visible when through flow is used at 6 L.min⁻¹, which suggests there may be some selective removal of the sebum.

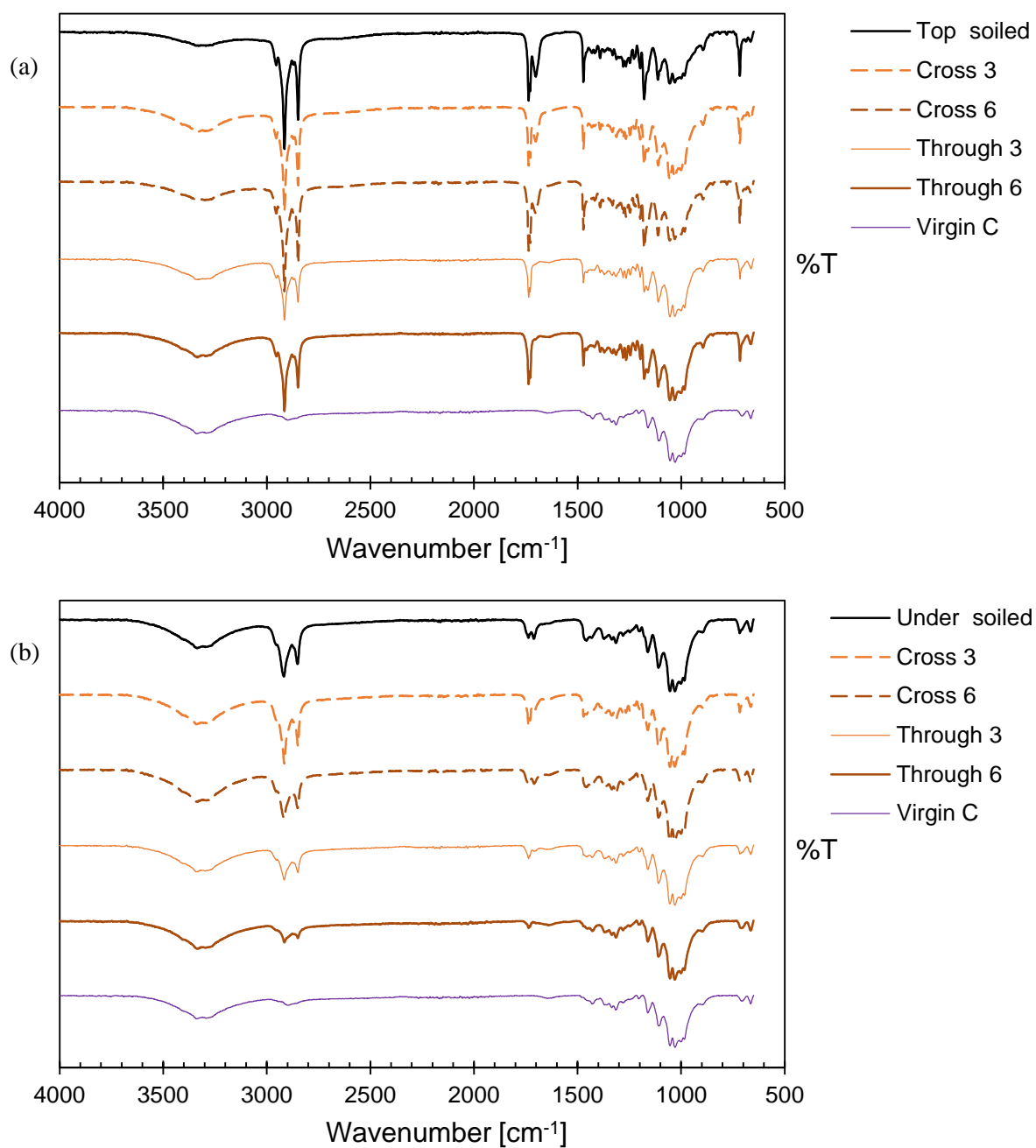


Figure 6.18. FTIR of cotton soiled with sebum cleaned using the flow rig at 40 °C with surfactant at a concentration of 2 x CMC. Four flow regimes were used comprising of cross and through flow, and 3 and 6 L.min⁻¹. This is compared to soiled and virgin polyester for both the (a) top and (b) underside of the fabric.

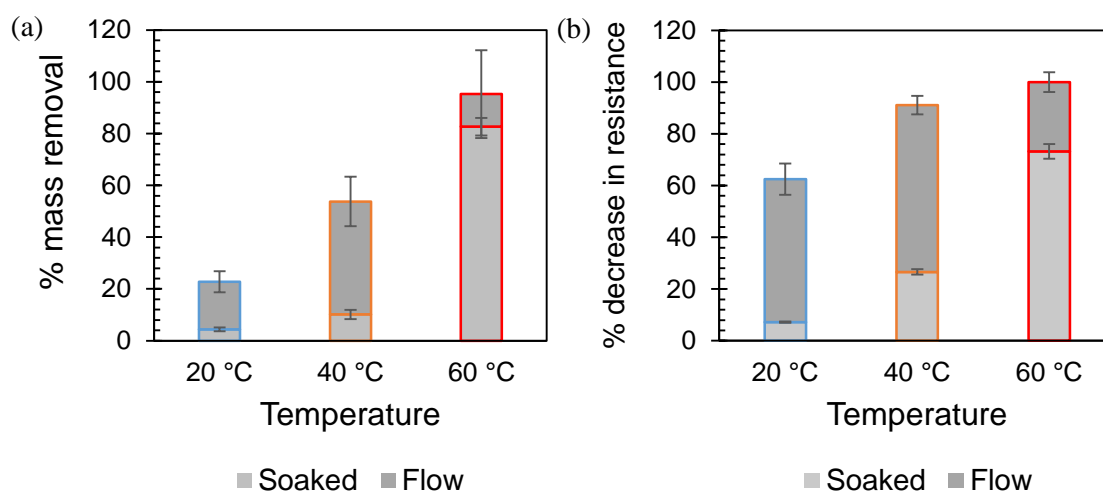
Flow conditions

The highest removal is seen for through flow at 6 L.min⁻¹, which also shows the most removal for polyester. The same conditions will be used when performing experiments with cotton.

6.1.2.2. Effect of Temperature

Mass, colour and resistance measurements

Figure 6.19 shows, as expected, increased removal of sebum is observed with increased temperature. The increase observed for fabric subjected to flow at 60 °C when compared to cotton soaked in the same conditions is small, but this may be due to the fact that removal is already very high when soaking alone is considered. The increased mass loss and improvement in colour is higher for 40 °C experiments than 20 °C, which is explained by the fact that wash solution at 40 °C will cause the sebum to be molten which will aid removal. The additional decrease in resistance when flow is used for cleaning is approximately the same for the two temperatures, which suggests cleaning from inside the pores is due to the flow of water forcing sebum out, whereas cleaning on the surface is more temperature dependant.



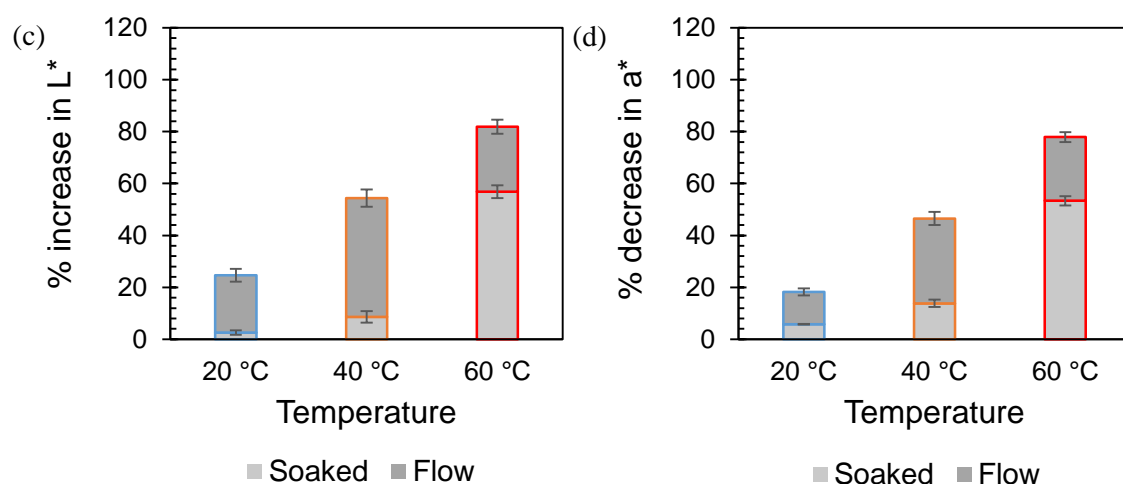


Figure 6.19. Effect of temperature on cleaning by the flow rig for cotton soiled with sebum. Surfactant was used at a concentration of 2 x CMC. Cleaning is measured by (a) % mass removal, (b) % decrease in resistance, (c) % increase in L^* and (d) % decrease in a^* . The error bars represent \pm one standard deviation for three fabrics. Five measurements were taken from each fabric for colour and resistance.

Colour of top and underside of fabric

Removal from the underside of the cotton is less than removal from the topside, as shown in Figure 6.20. This is likely to be because the wash solution travels over the topside of the fabric causing removal before going through the pores. Some sebum may also be transported from the topside to the underside without being fully removed, although this mechanism occurs to a lesser extent when surfactant is used at twice the CMC as in this case.

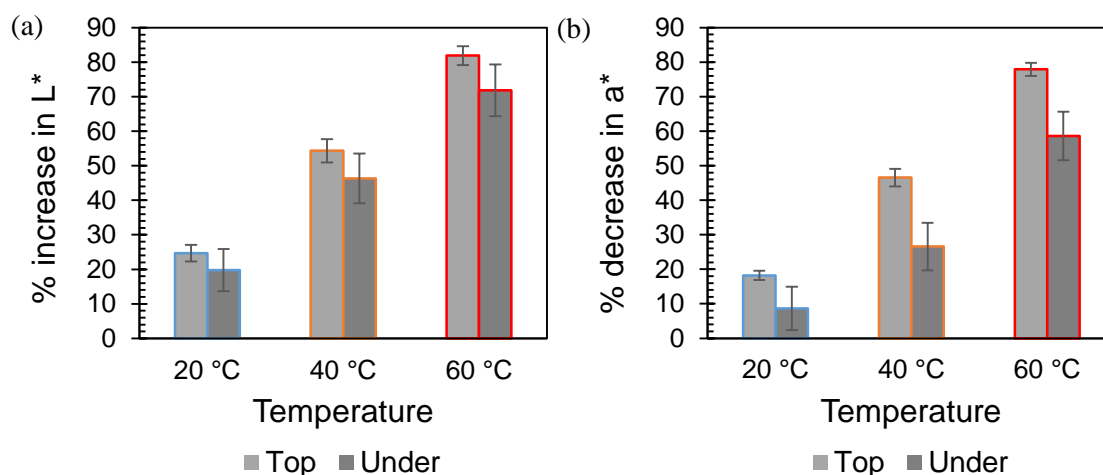


Figure 6.20. Comparison of the colour of the top and underside of cotton soiled with sebum cleaned using the flow rig at 20 °C, 40 °C and 60 °C with surfactant at a concentration of 2 x CMC. Colour is measured as (a) L* and (b) a*. The error bars represent \pm one standard deviation for three fabrics. Five measurements were taken from each fabric.

Mass per unit area

Figure 6.21 shows the mass per unit area measurements performed on cotton fabrics subject to flow at different temperatures. For 60 °C the central strip where flow is directed shows significant removal, almost to the level of virgin cotton. It can also be seen that the adjacent soiled strip also shows large amount of removal, although somewhat less than the central strip. It is likely that the heat of the wash solution has caused the sebum in these areas to liquefy, allowing removal to occur. The same trend is observed for the wash solution at 40 °C, although removal from both areas is less. This is likely to be due to the fact that the sebum has begun to melt though may not be fully liquefied. At 20 °C some removal is seen from the central strip of the fabric, but no removal is seen from the adjacent soiled area. This supports the mechanism that the sebum is removed at the other two temperatures as it has melted, which is not the case at 20 °C, where the sebum will be a waxy solid. For all three samples no spreading of the sebum is observed on to the clean area of the fabric.

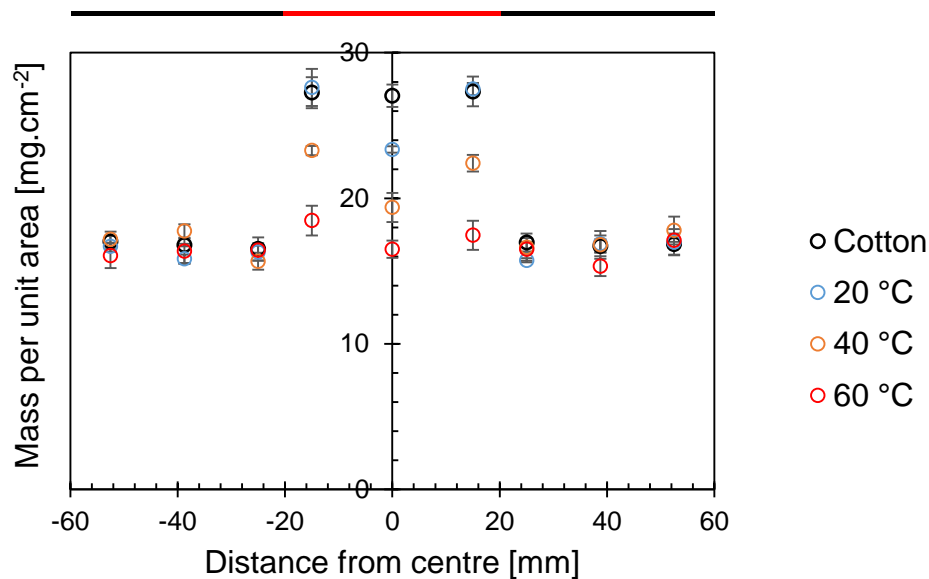


Figure 6.21. Mass per unit area of cotton soiled with sebum cleaned using the flow rig at 20 °C, 40 °C and 60 °C with surfactant at a concentration of 2 x CMC. The error bars represent \pm one standard deviation for three fabrics.

FTIR

FTIR spectra, presented in Figure 6.22, show removal is lowest at 20 °C, where the spectrum looks very similar to soiled cotton, and increases as temperature increases. Sebum peaks at 2900 and 2820 cm^{-1} decrease in size as the temperature is increased on both the topside and underside of the fabric. The sebum peak around 1740 cm^{-1} is not even visible when the fabric is washed at 60 °C. This supports previous results presented in this section.

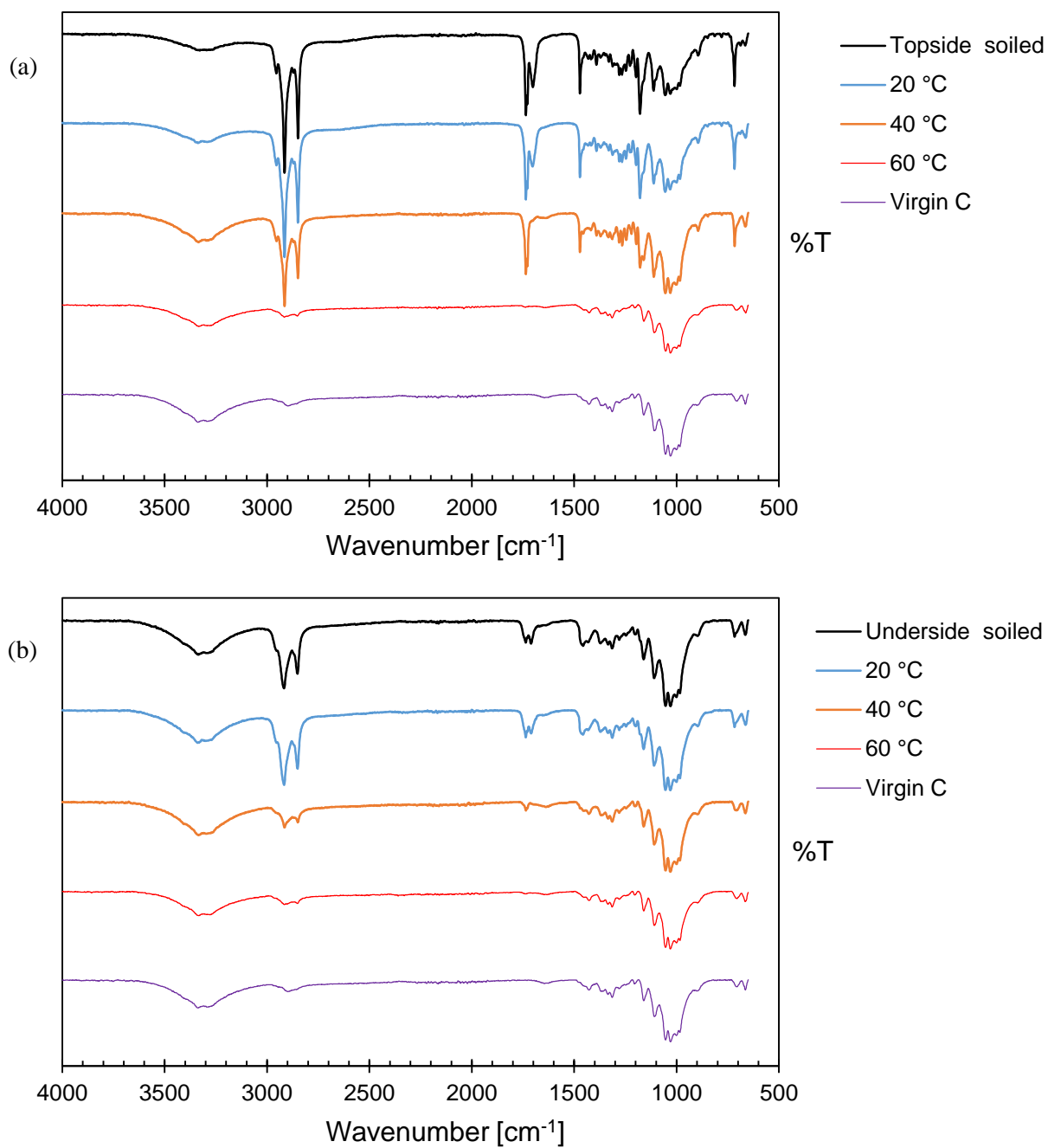
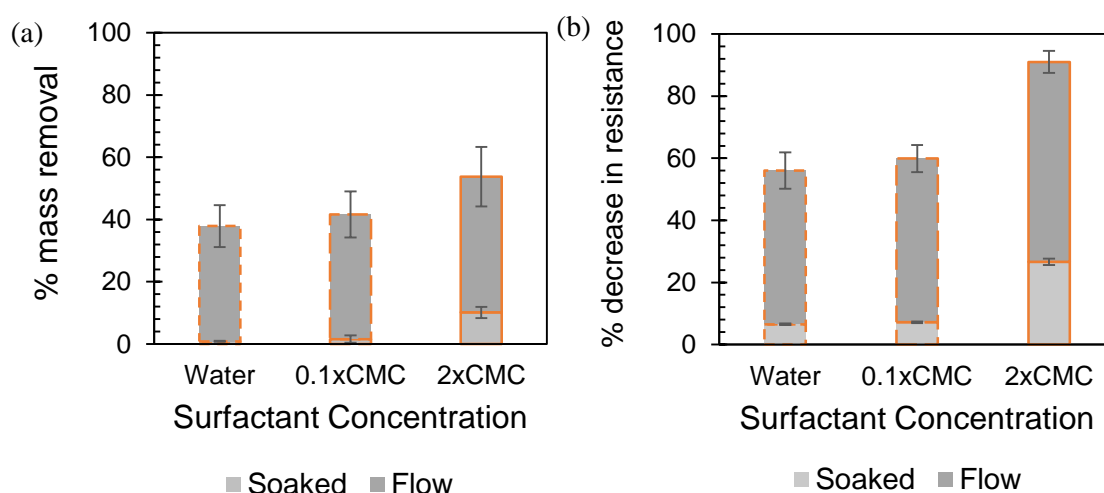


Figure 6.22. FTIR of cotton soiled with sebum cleaned using the flow rig at 20 °C, 40 °C and 60 °C with surfactant at a concentration of 2 x CMC. This is compared to soiled and virgin cotton for both the (a) top and (b) underside of the fabric.

6.1.2.3. Effect of surfactant concentration at 40 °C

Mass, colour and resistance measurements

When different concentrations of surfactant are used at 40 °C no significant increase in cleaning can be seen when 0.1 times the CMC of the surfactant is used when compared to water alone, as shown in Figure 6.23. However, a significant increase in cleaning is seen when twice the CMC is used. This suggests that mechanisms of cleaning below the CMC, roll up and emulsification, are not very effective under these conditions, and cleaning occurs by solubilisation, which is only possible above the CMC (Shaeiwitz et al., 1981). It can also be seen that the increase in cleaning when compared to soaking alone is very similar for all three conditions, suggesting there is no synergistic effect of using flow with chemical action under these conditions.



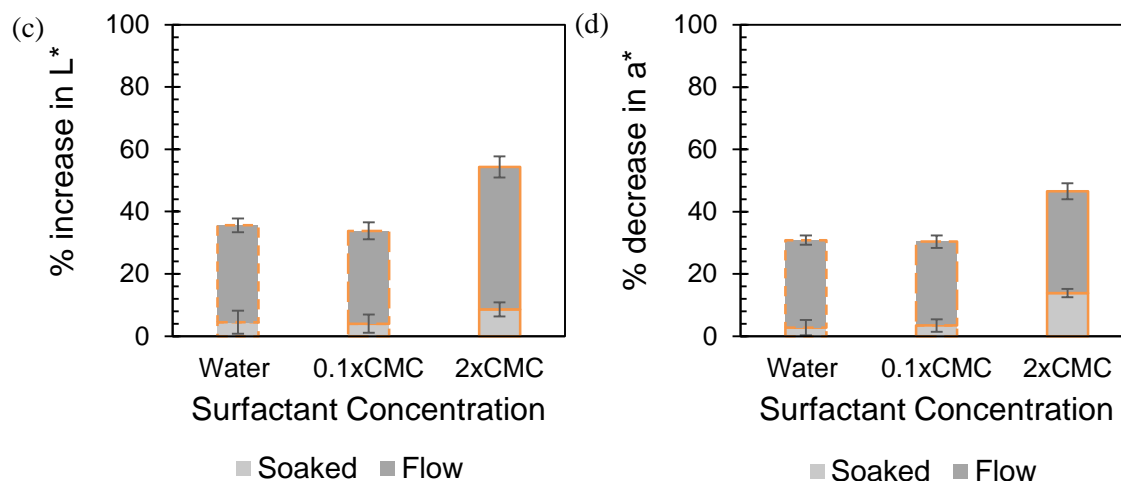


Figure 6.23. Effect of surfactant concentration on cleaning by the flow rig at 40 °C for cotton soiled with sebum. Cleaning is measured by (a) % mass removal, (b) % decrease in resistance, (c) % increase in L^* and (d) % decrease in a^* . The error bars represent \pm one standard deviation for three fabrics. Five measurements were taken from each fabric for colour and resistance.

Colour of top and underside of fabric

Figure 6.24 shows that removal from the underside of the fabric is significantly less than removal from the topside of the fabric for all three conditions, although some removal is seen from the underside for all fabrics. It is likely that this is because the flow over the top surface causes some removal before the flow is directed through the pores, but the same does not occur on the underside. Of the three samples when twice the CMC is used the removal from the underside is most similar to the topside. This may be because the surfactant aids removal of the sebum from the fabric, allowing it to be carried away in the wash solution. Without that level of surfactant the oily sebum is not suspended in the wash solution and as such remains on the fabric.

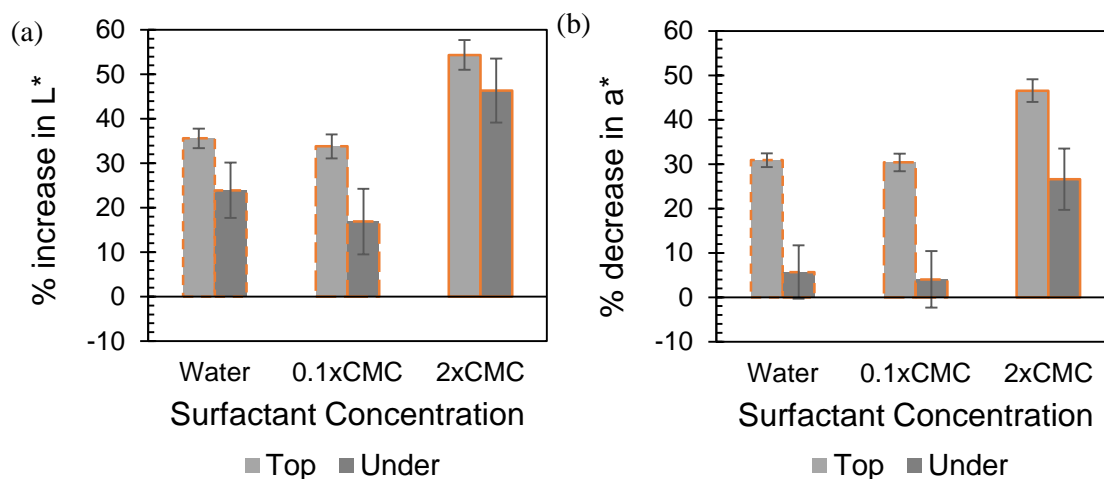


Figure 6.24. Comparison of the colour of the top and underside of cotton soiled with sebum cleaned using the flow rig at 40 °C with water and surfactant at a concentration of 0.1 x and 2 x CMC. Colour is measured as (a) L* and (b) a*. The error bars represent \pm one standard deviation for three fabrics. Five measurements were taken from each fabric.

Mass per unit area

Mass per unit area results, shown in Figure 6.25, show for all samples mass loss is greatest from the central strip of the fabric. Mass loss is also found to be in line with surfactant concentration, with the most removal found when twice the CMC is used and the least removal found with water, although the difference between water and 0.1 times the CMC is small. Removal from the adjacent strip on the soiled area is less than the central strip, but is highest when the surfactant level is highest. This may be because the surfactant in the wash solution is able to penetrate the fabric in this area and aid removal of the sebum, similar to soaking the fabric. The clean strip adjacent to the soiled area doesn't increase in mass, which indicates that the sebum has not spread in to this area.

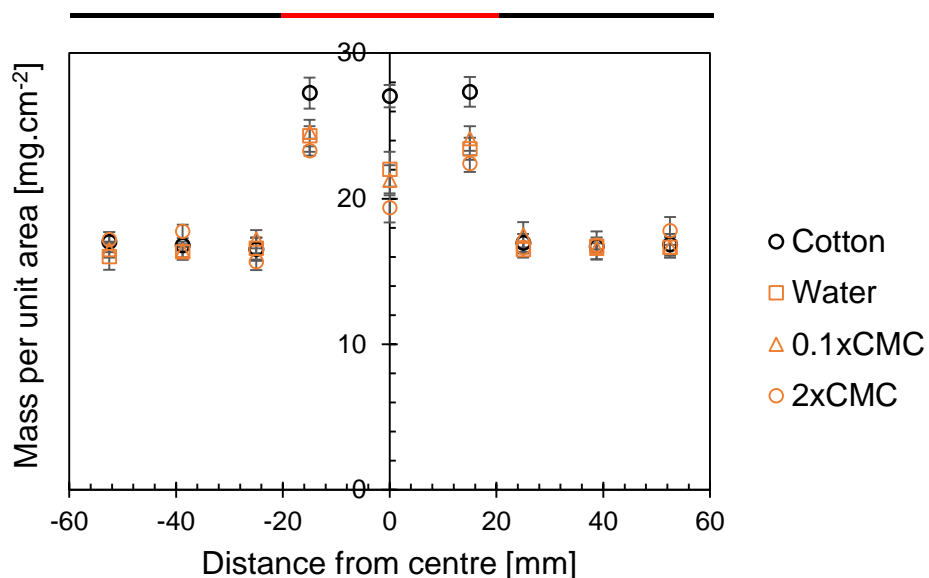


Figure 6.25. Mass per unit area of cotton soiled with sebum cleaned using the flow rig at 40 °C with water and surfactant at a concentration of 0.1 x and 2 x CMC. The error bars represent \pm one standard deviation for three fabrics.

FTIR

Figure 6.26 shows FTIR spectra for the three surfactant concentrations compared to soiled and virgin fabrics. Some reduction in the sebum peaks at 2900 and 2830 cm^{-1} can be seen on the topside of the fabric under all three conditions. On the underside of the fabric significant reduction in the size of these peaks can only be seen when twice the CMC is used. This is in line with removal data presented previously, in particular the colour of the topside and underside of the fabrics.

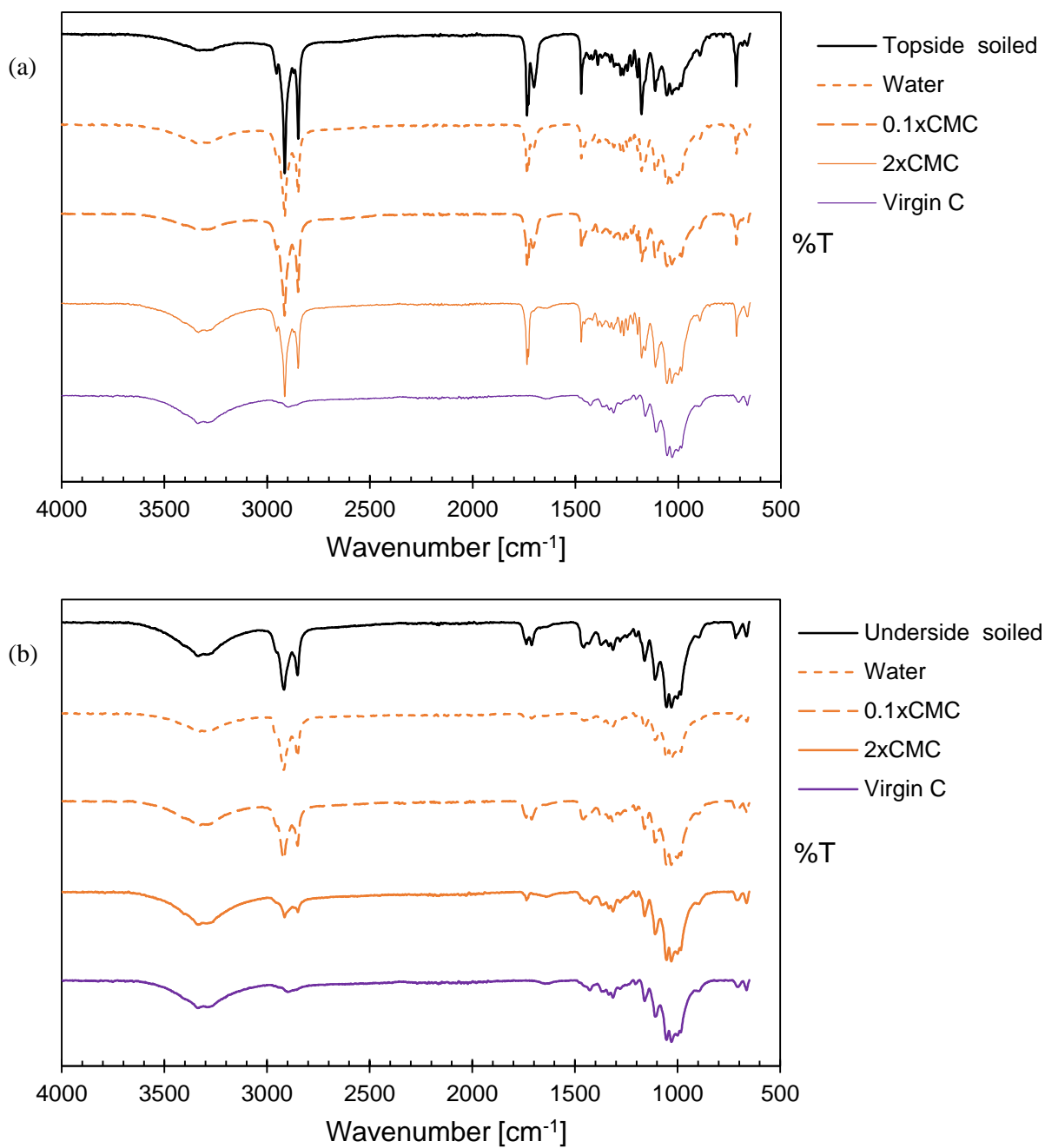
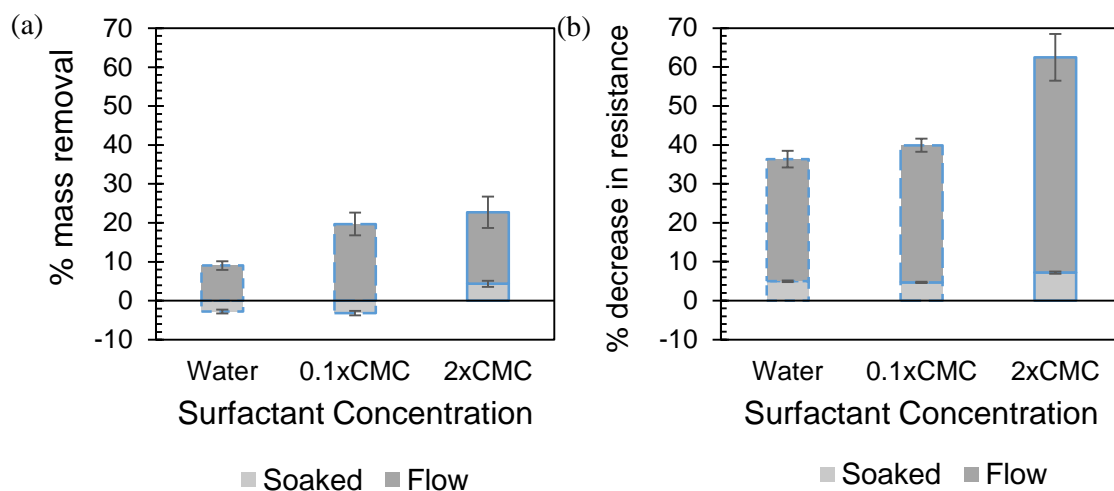


Figure 6.26. FTIR of cotton soiled with sebum cleaned using the flow rig at 40 °C with water and surfactant at a concentration of 0.1 x and 2 x CMC. This is compared to soiled and virgin cotton for both the (a) top and (b) underside of the fabric.

6.1.2.4. Effect of surfactant concentration at 20 °C

Mass, colour and resistance measurements

Figure 6.27 shows that for cotton at 20 °C removal of sebum is significantly higher when twice the CMC of the surfactant is used. Some benefit is seen for mass and colour loss when 0.1 times the CMC is used compared to water alone. This benefit is not seen for resistance, where there is no difference between the two conditions. This suggests that surfactant is aiding removal of sebum from the top surface even at low concentration, but that to aid removal from the pores requires a higher concentration of surfactant. The force of the water causes the removal from the pores at low concentration, but some synergistic effect is seen between the surfactant and the flow of wash solution at the higher concentration, as the increase in cleaning compared to soaking alone is much higher.



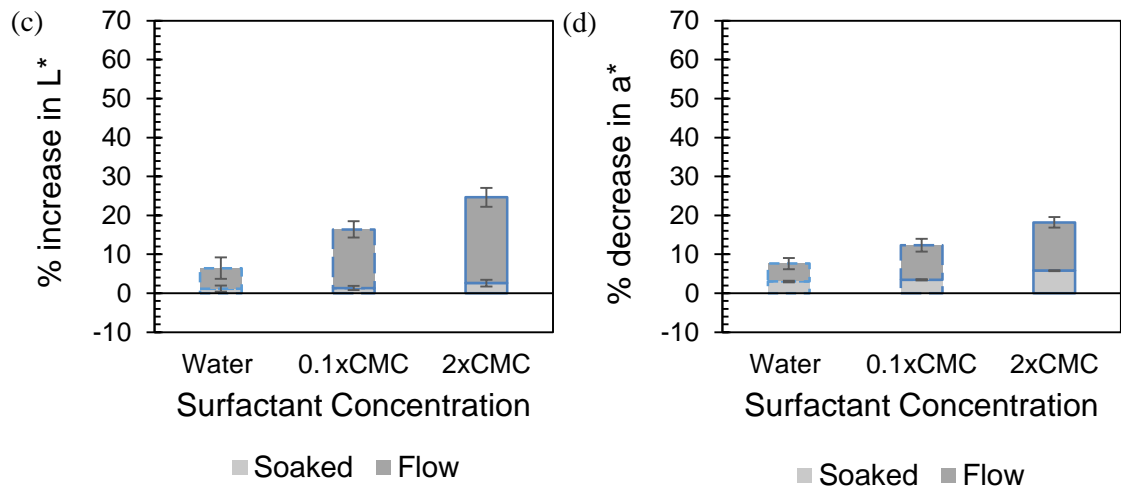


Figure 6.27. Effect of surfactant concentration on cleaning by the flow rig at 20 °C for cotton soiled with sebum. Cleaning is measured by (a) % mass removal, (b) % decrease in resistance, (c) % increase in L^* and (d) % decrease in a^* . The error bars represent \pm one standard deviation for three fabrics. Five measurements were taken from each fabric for colour and resistance.

Colour of top and underside of fabric

When the colour of the topside and underside of the fabric are considered, as in Figure 6.28, it can be seen that the underside of the fabric washed in 20 °C water is actually more dirty than the original soiled fabric. This suggests that the water is flowing through the pores and removing sebum from them but depositing the sebum on the underside of the fabric since there is no surfactant to suspend it in the wash solution. This is not that case when surfactant is used, and the underside of the fabric has been cleaned almost to the same extent as the top surface.

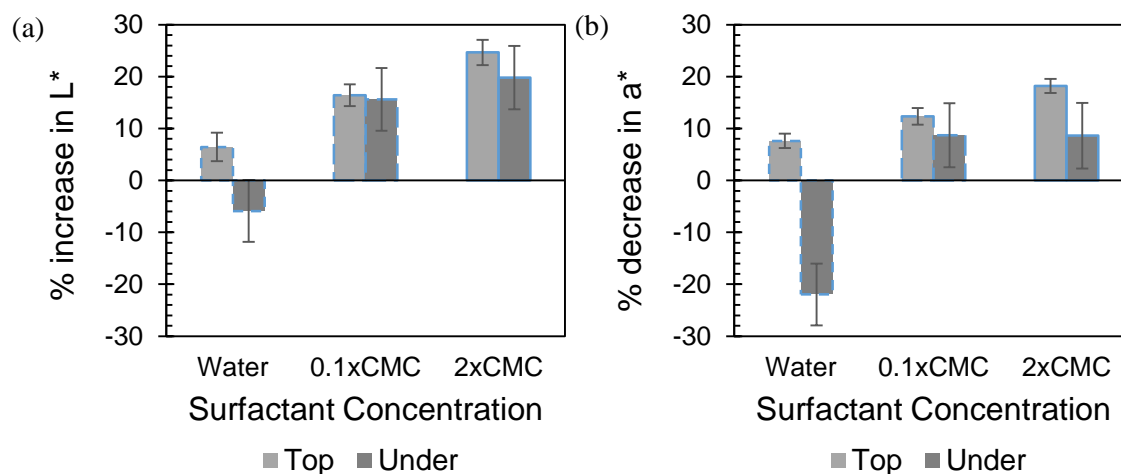


Figure 6.28. Comparison of the colour of the top and underside of cotton soiled with sebum cleaned using the flow rig at 20 °C with water and surfactant at a concentration of 0.1 x and 2 x CMC. Colour is measured as (a) L^* and (b) a^* . The error bars represent \pm one standard deviation for three fabrics. Five measurements were taken from each fabric.

Mass per unit area

It can be seen in Figure 6.29 that the mass is lost from the fabric is almost entirely from the central strip, which is subject to the flow of wash solution. The highest loss can be seen for twice the CMC of the surfactant, with some loss observed for 0.1 times the CMC. No significant mass loss is observed for when water is used. Removal from the adjacent strips is not significant for any of the conditions, and no spreading of the sebum is seen onto the adjacent clean area of cotton.

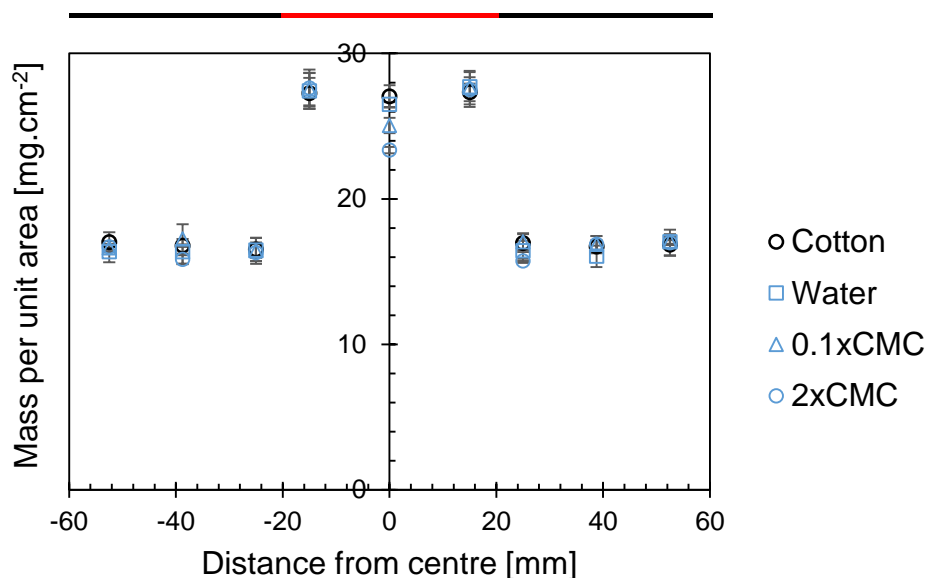


Figure 6.29. Mass per unit area of cotton soiled with sebum cleaned using the flow rig at 20 °C with water and surfactant at a concentration of 0.1 x and 2 x CMC. The error bars represent \pm one standard deviation for three fabrics.

FTIR

Figure 6.30 shows the FTIR for the fabrics washed with flow at 20 °C. It can be seen that on the topside the sebum peaks appear to be the same size for all three fabrics, and the same as the soiled cotton. However the cotton peak at 3300 cm^{-1} is more distinctive when twice the CMC is used suggesting more sebum has been removed exposing the surface of the cotton to a greater extent. The underside of the fabric shows the same trend. It is expected that the samples show more similarity to the soiled sample than to the virgin cotton since mass removal is below 25% for all three samples.

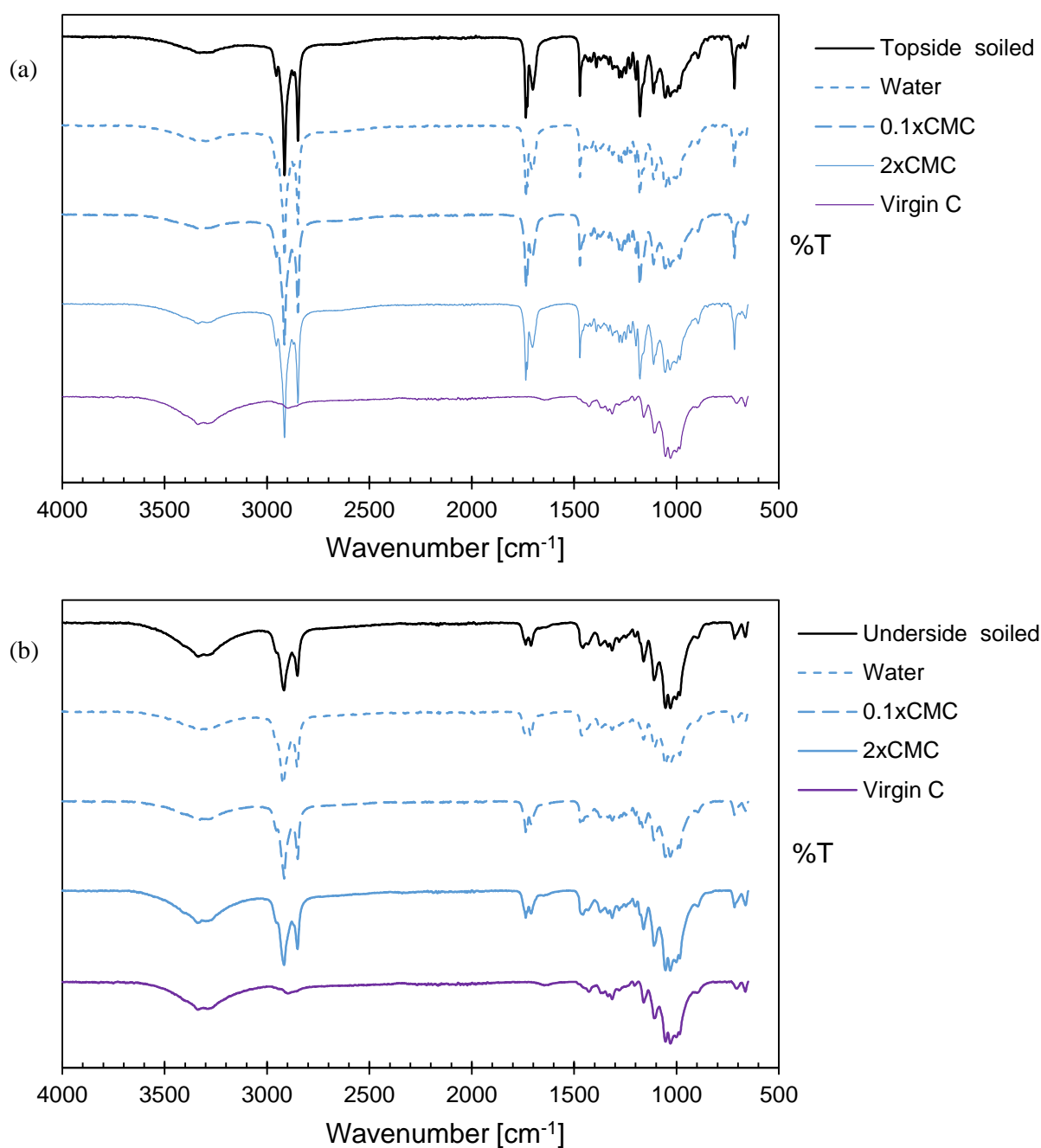


Figure 6.30. FTIR of cotton soiled with sebum cleaned using the flow rig at 20 °C with water and surfactant at a concentration of 0.1 x and 2 x CMC. This is compared to soiled and virgin cotton for both the (a) top and (b) underside of the fabric.

6.1.3. Discussion on flow

For both fabrics maximum removal was found when through flow was used at 6 L.min⁻¹ when tested at 40 °C with twice the CMC of the surfactant. This fits with intuition, as it would be expected that

water passing through the pores of the fabric would remove more of the sebum in the pores, but would also remove sebum on the surface since it passes over the surface. It also makes sense that a higher flow rate causes greater removal, since this will provide greater force to remove sebum in the pores, and since the fabric will be exposed to twice the volume of surfactant solution. Interestingly, for polyester, when cross flow is used greater removal is seen when the lower flow rate, $3 \text{ L}\cdot\text{min}^{-1}$, is used. It is suspected that the higher flow rate, as it passes over the surface of the fabric, is pushing some of the sebum further into the pores of the fabric because of the increased shear force. This trend is not seen for cotton, which may be due to the fact that there is significantly less sebum on the cotton fabric so there is less to force into the fabric. It may also be due to the fact that, on average, the cotton pores are larger than the polyester pores meaning less sebum is trapped. The data supports this, polyester fabrics with cross flow show no benefit in change in resistance over soaking alone, whereas cotton fabric show a significant benefit.

When we consider different temperatures at the optimal flow rate it can be seen that removal increases with temperature for both fabrics. For mass and colour change for polyester, the additional benefit when compared to soaking alone is much greater at 60°C , however the benefit for resistance is equal at the three temperatures. This suggests the flow of water removes sebum from the pores irrespective of temperature. Removal from the surface is aided by the increased temperature, which will cause the sebum to be more liquefied and therefore easier to remove. For cotton, the additional benefit of flow on resistance is equivalent at the two lower temperatures, but is less at 60°C . This is because removal at this temperature is already high so an equivalent benefit would not be possible. Mass and colour results show a much larger benefit when 40°C surfactant solution is used, which is likely to be because of the phase that the sebum will be in at that temperature. For both fabrics, cleaning on the surface appears to be much more dependent on temperature than cleaning from the pores.

For 20°C and 40°C on both fabrics a benefit is seen when twice the CMC is used, suggesting a synergistic effect between the flow of water and surfactant concentration. It is thought that as the

surfactant solution passes over the fabric the surfactant is able to remove the soil by mechanisms such as solubilisation and emulsification, and the removed soil is then washed away by the flow of water. These mechanisms are not possible without surfactant at a concentration above the CMC. Resistance results show the greatest improvement, which is likely to be because the through flow of water has forced sebum from the pores. At 40 °C no real benefit is seen when using 0.1 times the CMC of the surfactant when compared to water alone. At 20 °C on polyester the lower concentration of surfactant has a small negative effect on cleaning when compared to water. Conversely, a small but significant benefit is seen when the lower concentration of surfactant is used with cotton. The difference is likely to be due to the way the sebum attaches to the surface of the fabric, since at 20 °C very little cleaning will be due to a change in phase of the sebum. It may be that, because the layer of sebum is thinner on cotton, penetration and therefore removal by the surfactant is easier, hence increased removal at lower concentrations.

6.2. Fluid Dynamic Gauging

6.2.1. Proof of concept

Initial FDG experiments were performed on polycotton fabric soiled using method 1 described in section 3.1.2.1. The gauge set up involved the syringe pump, which has a maximum flow rate of 80 mL.min⁻¹. A weight of 380 g was attached to the fabric and allowed to hang over the edge of the platform to tension the fabric. FDG was carried out in water at 20 °C and 40 °C. Figure 6.31 shows (a) the appearance of the nozzle footprint on the fabric during the experiment, (b) the topside of the fabric and (c) the underside of the fabric. It can be seen that the underside of the fabric is almost completely cleaned, while the topside of the fabric had a clear footprint of the nozzle with additional red sebum. This suggests sebum is being removed from the underside of the fabric through the pores of the fabric and remaining on the top surface. To further investigate this microscope images and L* and a* colour readings were obtained.

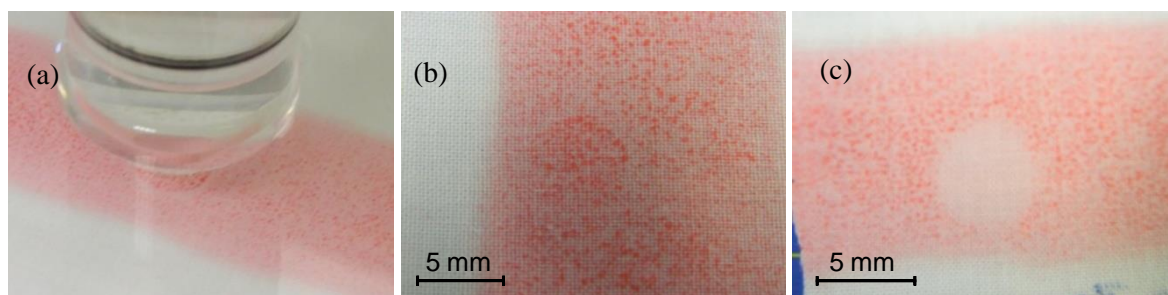


Figure 6.31. Images of gauged polycotton showing (a) the appearance of the nozzle footprint on the fabric during the experiment, (b) the topside of the fabric and (c) the underside of the fabric for an experiment performed at 40 °C in water.

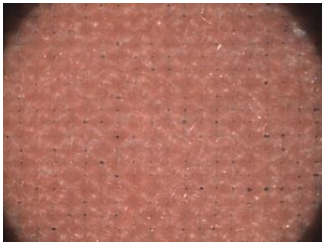

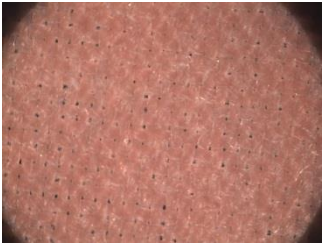

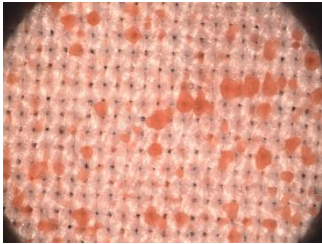

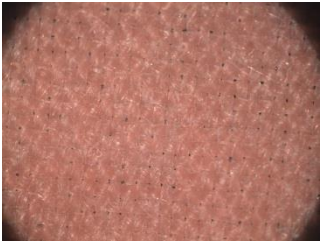
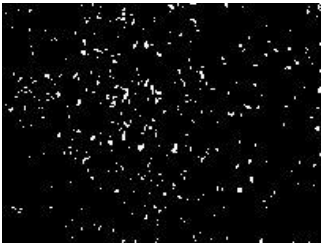
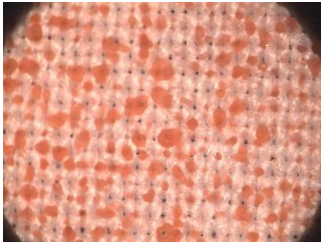
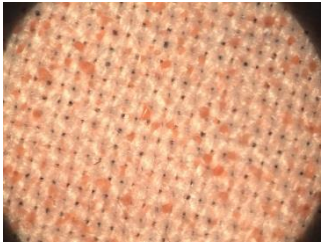
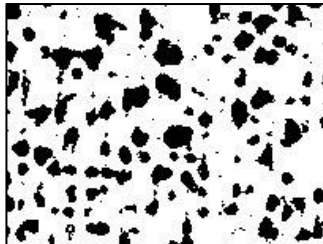

Microscope images

The gauged area was imaged by a microscope camera to show the colour change, as shown in Table 6.1. It can be seen that at 20 °C even at high shear stress there is very little change in the fabric. When the fabric is soaked at 40 °C it can be seen that some of the soil becomes detached from the fabric and pools on the surface. When shear stress is then applied to this we can see that the underside of the fabric becomes almost completely clean whereas more sebum collects on the top of the fabric. Again this supports the theory that sebum is being pulled through the pores of the fabric to the top surface.

Microscope images were also analysed using ImageJ. An area was selected avoiding the black corners. The image was then thresholded using the Colour Threshold Tool set to L*, a*, b*. Levels were set as L*= 177-211 and a*= 135-167 for each image, which selected red areas on the images without selecting pores. The total red area was then calculated and is presented in Table 6.2.

It can be seen that soaking the fabric at 20 °C and shear stress applied at this temperature have no noticeable effect on the amount of redness on the surface. When the fabric is soaked at 40 °C the redness reduces dramatically from 98.8% to 35.0%. When a low shear stress is then applied to this the top of the surface has fewer red areas, whereas the underside has a very small amount of red areas. If a larger shear stress is then applied the top surface actually has an increased amount of red areas, whereas the underside is almost completely clean.

Table 6.1 Microscope images of gauged polyester in 20 °C and 40 °C water at two different shear stresses.

	20 °C	40 °C
Soiled fabric		
Soaked fabric	 	 
$\tau = 2.5 \text{ Pa}$	 	<div>TopsideUnderside</div>    

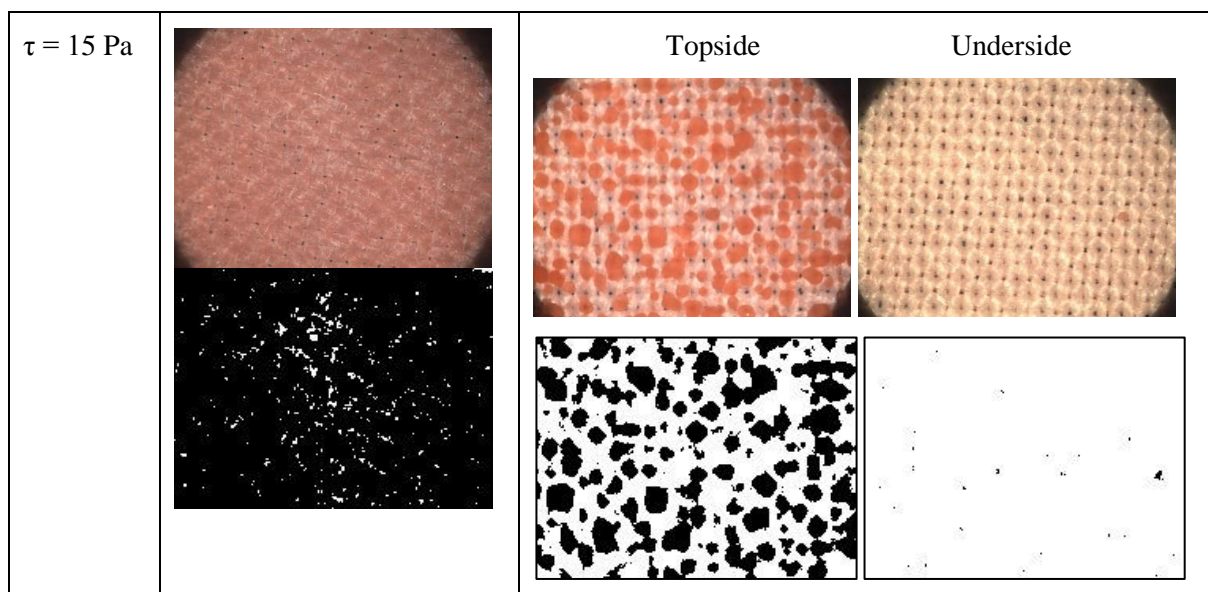


Table 6.2 Percentage area of microscope images defined as red by colour thresholding.

	20 °C	40 °C
Soiled Fabric	98.8%	
Soaked Fabric	97.1%	35.0%
$\tau = 2.5 \text{ Pa}$	97.3%	Topside: 24.0% Underside: 2.46%
$\tau = 15 \text{ Pa}$	96.9%	Topside: 39.9% Underside: 0.182%

Colour analysis

L^* and a^* readings were also obtained for the gauged areas. Rather than analysing red areas, these readings give an average colour for the entire gauged area. Figure 6.32 plots the difference between samples and soiled fabric in terms of (a) L^* and (b) a^* . An increase in L^* indicates an increase in lightness of colour, and a decrease in a^* gives a decrease in redness of the colour, both signifying removal of sebum from the surface. A small difference can be seen when the fabric is soaked in 20 °C water. No additional benefit is observed when shear stress is applied to the fabric. A much larger benefit is seen on both the topside and underside of the fabric when the fabric is soaked in 40 °C water. When low shear stress is then applied the top surface of the fabric becomes darker and redder,

whereas the back surface has been cleaned more. This effect is even more pronounced when high shear stress is applied. This supports the theory that the gauge has pulled the sebum from the underside of the fabric and deposited it on the top surface.

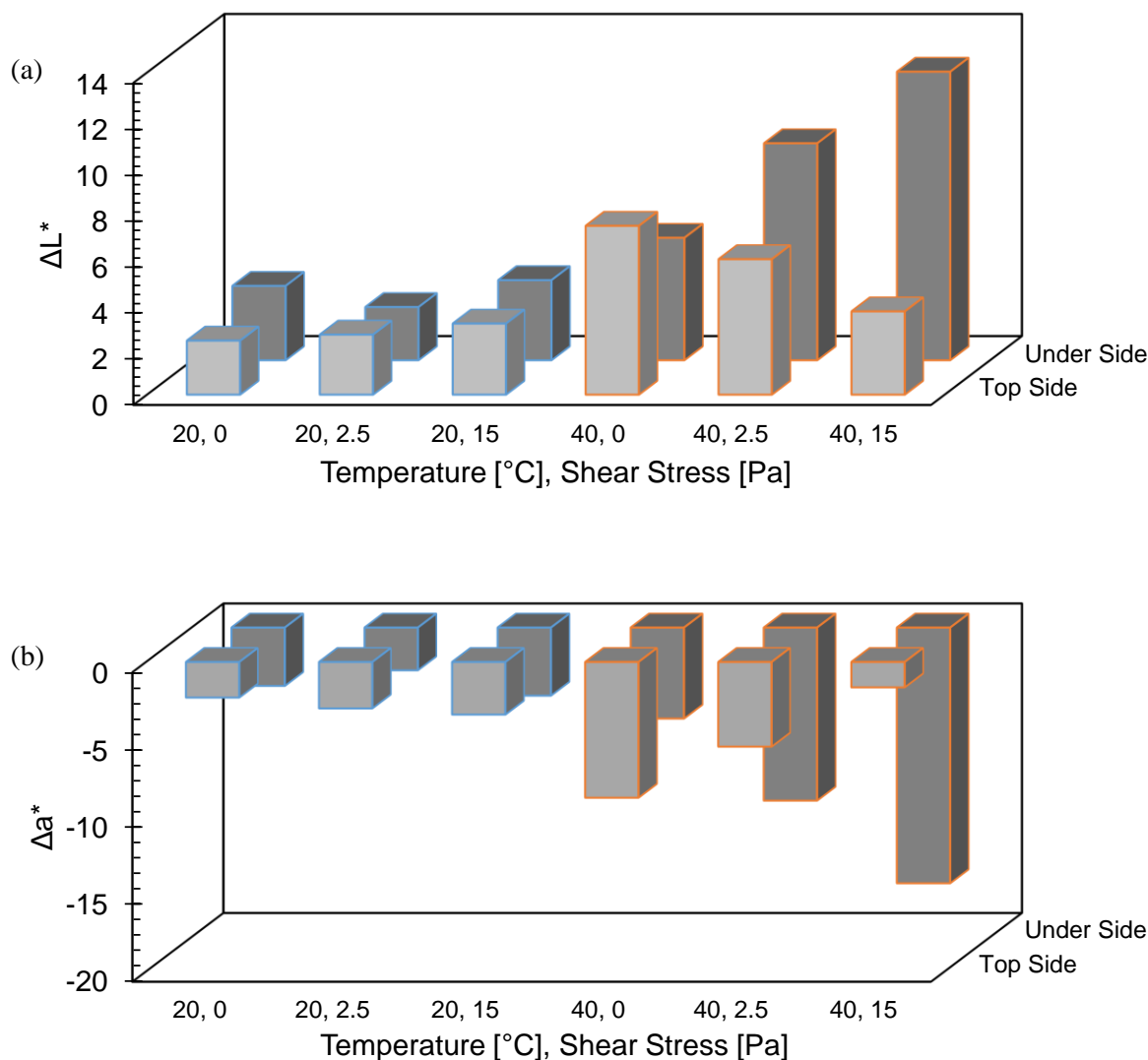


Figure 6.32. (a) ΔL^* and (b) Δa^* values for the top and underside of fabrics gauged in water at 20 °C and 40 °C with 0 Pa, 2.5 Pa and 15 Pa shear stress.

6.2.2. Polyester

FDG experiments were then performed on polyester soiled using application method 2 using the new gear pump and flow meter set up, which enabled the use of higher flow rates. Initially, a flow rate of 500 mL.min⁻¹ was used. It was found that the virgin polyester used to calibrate the gauge moved up

towards the nozzle when this higher flow rate was used. An additional two weights were used to tension the fabric, giving a total of 1125 g, as shown in Figure 3.20. It was found that the fabric still moved towards the nozzle so the flow rate was reduced to $100 \text{ mL}\cdot\text{min}^{-1}$, at which the fabric no longer moved and experiments were possible. Gauging was performed at two shear stresses, 10 Pa and 30 Pa. A large amount of removal was seen when twice the CMC was used in 60°C wash solution, and a small amount of removal was seen at 40°C , as shown in Figure 6.33. Significant removal could not be observed visually under any other conditions.

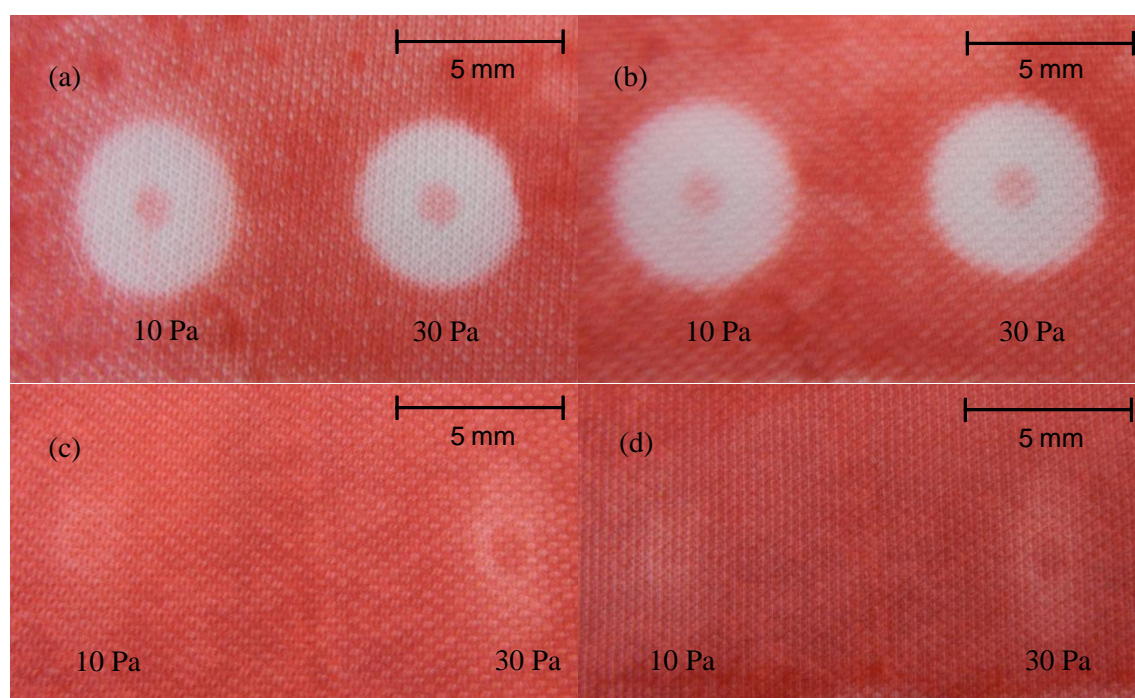


Figure 6.33. Images of gauged area of polyester showing (a, c) topside and (b, d) underside of fabrics in (a, b) 60°C and (c, d) 40°C surfactant solution at $2 \times \text{CMC}$.

It can be seen that removal has occurred from both the topside and underside of the fabrics. At 60°C it appears that this removal is almost equal, and that the fabric under the footprint of the nozzle is almost completely clean. This suggests sebum is being pulled from the underside of the fabric through the pores and is being completely removed from the top surface. There is no observable difference between the higher and lower shear stresses. This can be explained by the fact that sebum will be completely liquefied at this temperature and hence will be able to pass through the fabric easily when stress is applied. At 40°C it is obvious that removal is higher at the higher shear stress,

which is explained by the fact that the sebum will be molten at this point but won't be fully liquefied. This means it won't be as penetrative as it is at the higher temperature, and hence increasing the shear stress will have a greater effect.


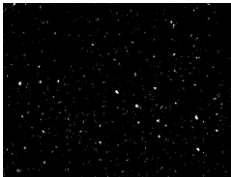

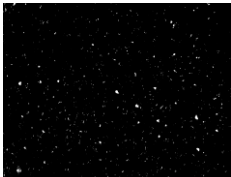

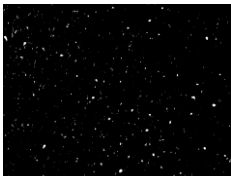

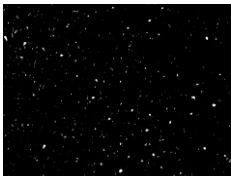







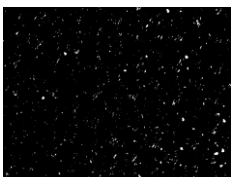

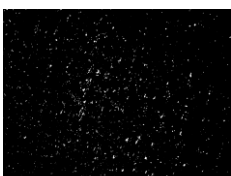
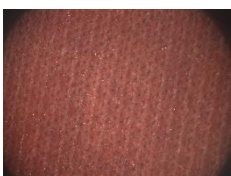


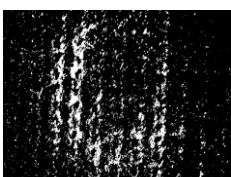
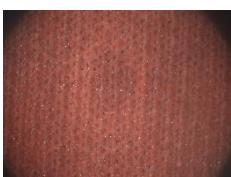
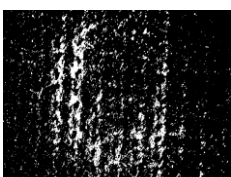
To further investigate this microscope images and L^* and a^* colour readings were obtained for all conditions. Again, microscope images were analysed using ImageJ. The central area of the image, where gauging occurred, was selected avoiding the corners. The image was then thresholded using the Colour Threshold Tool set to L^* , a^* , b^* . For these samples levels were set as $L^* = 140-210$ and $a^* = 132-162$ for each image, which selected red areas on the images without selecting pores or white areas. The total red area was then calculated and is presented as percentage coverage. L^* and a^* values were also obtained using the spectrophotometer to give the averaged colour of the gauged area.


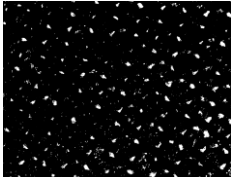

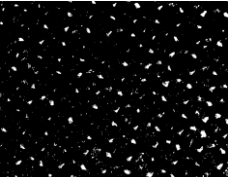
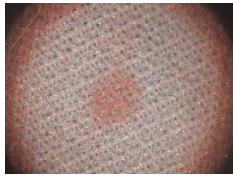
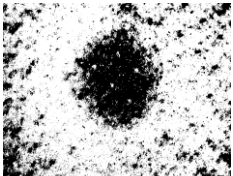
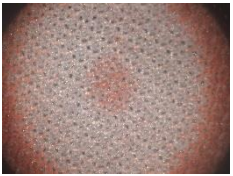
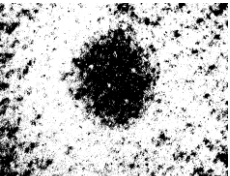

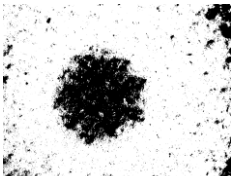

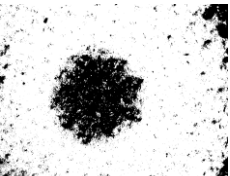
6.2.2.1 Effect of temperature

Microscope images

Microscope images for a range of temperatures when twice the CMC is used are presented in Table 6.3. No differences can be seen between any of the conditions at 20 °C. The sebum is still a waxy solid at this temperature and as such is not removed from the topside or underside even with a high shear stress. At 40 °C a difference is only seen when high shear stress is used, and the visual difference observed in Figure 6.33 at low shear stress is not found when the image is thresholded. Removal is on par from both the topside and underside, and can be seen to form the shape of the footprint of the nozzle, as would be expected. Removal is much higher at 60 °C, in line with what is observed previously. There is a noticeable difference between the low and high shear stress, showing the importance of using higher force to remove sebum.

Table 6.3. Microscope images of gauged polyester at 20 °C, 40 °C and 60 °C at twice the CMC.

	Topside Image	Topside ImageJ	Underside Image	Underside ImageJ
20 °C 2 x CMC Soaked		 Coverage:98.9%		 Coverage:98.5%
20 °C 2 x CMC 10 Pa		 Coverage: 99.0%		 Coverage: 98.7%
20 °C 2 x CMC 30 Pa		 Coverage: 98.5%		 Coverage: 98.1%
40 °C 2 x CMC Soaked		 Coverage:99.0%		 Coverage:98.4%
40 °C 2 x CMC 10 Pa		 Coverage:98.4%		 Coverage: 98.2%
40 °C 2 x CMC 30 Pa		 Coverage:88.6%		 Coverage:88.3%

60 °C 2 x CMC Soaked		 Coverage:95.4%		 Coverage:95.5%
60 °C 2 x CMC 10 Pa		 Coverage: 27.6%		 Coverage: 27.6%
60 °C 2 x CMC 30 Pa		 Coverage:18.1%		 Coverage:17.7%

Colour analysis

Figure 6.34 shows percentage changes in L^* and a^* after gauging. It can be seen that at 60 °C removal is equal on both the topside and underside of the fabric under all conditions. Removal at 60 °C is also higher than at other temperatures, which is to be expected as the sebum will have liquefied at this temperature therefore will be much easier to remove when force is applied using the gauge. It can be seen that when 40 °C wash solution with twice the CMC of surfactant is used, removal is actually higher on the underside of the fabric than the topside. This suggests that sebum is being pulled from the underside of the fabric through the pores. Some removal is seen on the top of the fabric, but less than the underside which may be due to the increased concentration of sebum after some has been pulled from the underside. Removal is very low at 20 °C, which is as expected as the sebum is a waxy solid at this temperature. Some removal is seen from the topside, with none seen from the underside. The sebum is not able to pass through the fabric at this temperature.

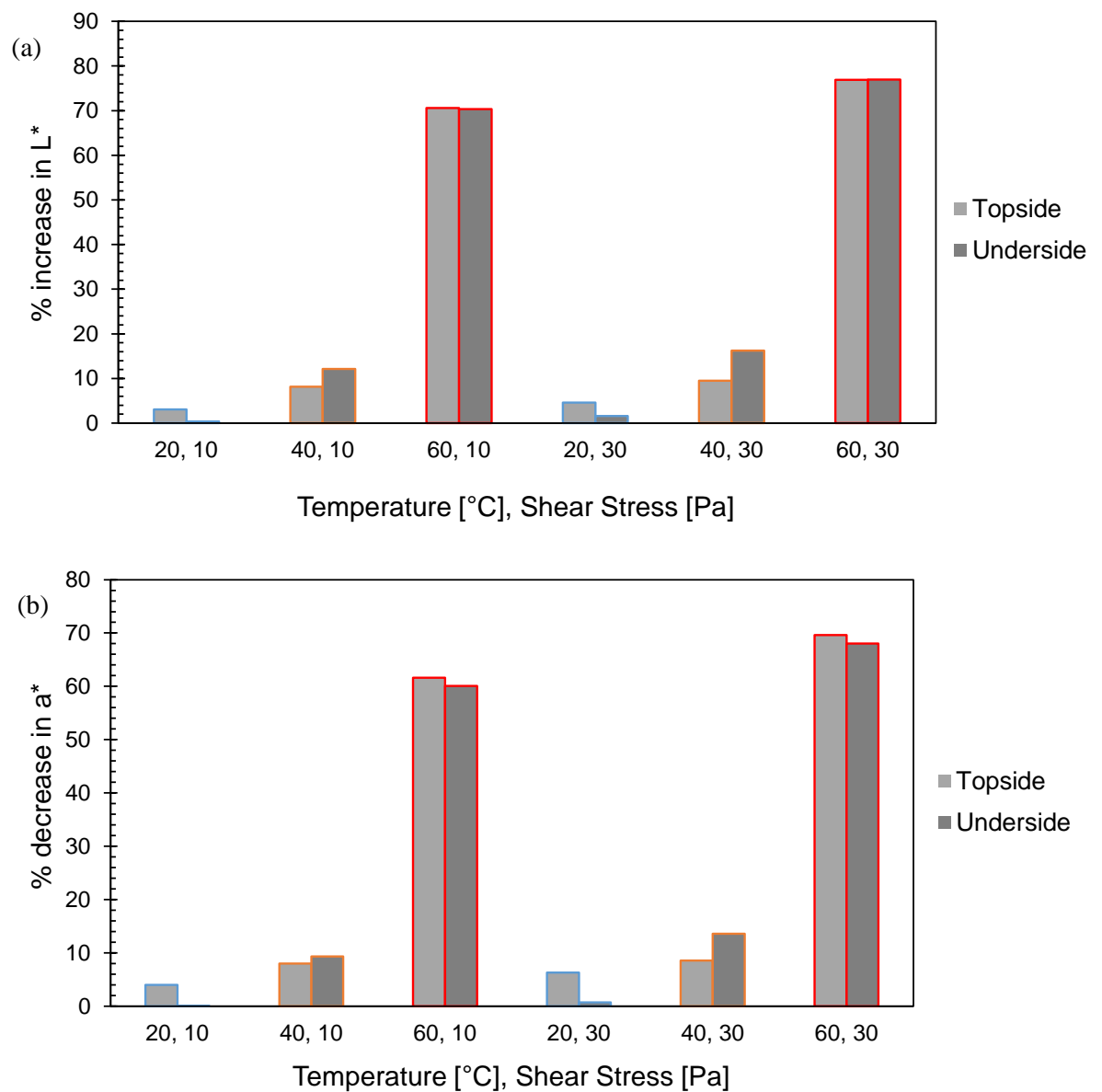


Figure 6.34. (a) Percentage increase in L^* and (b) percentage decrease in a^* when shear stresses of 10 Pa and 30 Pa are used in wash solution at a concentration of 2 x CMC of the surfactant at 20 °C, 40 °C and 60 °C.


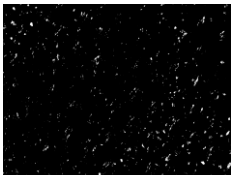

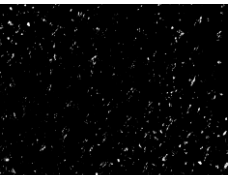



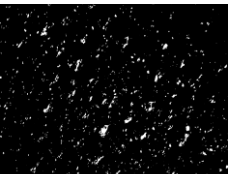
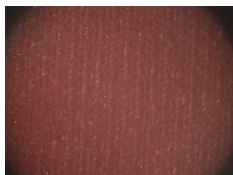


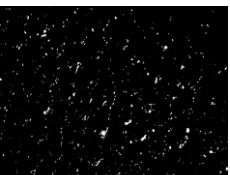
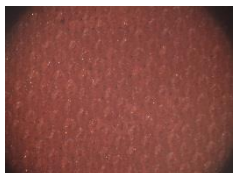
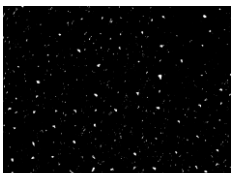






6.2.2.2. Effect of surfactant concentration at 40 °C








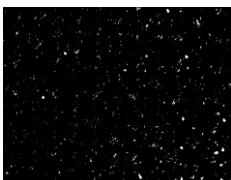





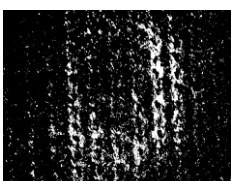

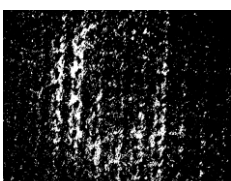
Microscope images

At 40 °C removal is only seen when the gauge is used with twice the CMC of surfactant, as shown in Table 6.4. Removal is low at low shear stress, and ImageJ is not able to detect this difference when the image is thresholded. Some removal is seen at higher shear stress, and ImageJ shows the footprint

of the nozzle on both the topside and underside of the fabric. These results show that not only is a higher temperature required but surfactant at a concentration above its CMC is also needed to aid removal of sebum. The surfactant does this by solubilising the sebum in the wash solution allowing transport away from the fabric surface.

Table 6.4. Microscope images of gauged polyester at 40 °C with water and surfactant at a concentration of 0.1 x and 2 x CMC.

	Topside Image	Topside ImageJ	Underside Image	Underside ImageJ
40 °C Water Soaked		 Coverage: 98.3%		 Coverage: 98.2%
40 °C Water 10 Pa		 Coverage:97.2%		 Coverage:96.7%
40 °C Water 30 Pa		 Coverage:97.2%		 Coverage:97.8%
40 °C 0.1 x CMC Soaked		 Coverage: 98.7%		 Coverage: 98.1%
40 °C 0.1 x CMC 10 Pa		 Coverage:98.1%		 Coverage: 98.4%

40 °C 0.1 x CMC 30 Pa		 Coverage:97.0%		 Coverage:97.3%
40 °C 2 x CMC Soaked		 Coverage:99.0%		 Coverage:98.4%
40 °C 2 x CMC 10 Pa		 Coverage:98.4%		 Coverage: 98.2%
40 °C 2 x CMC 30 Pa		 Coverage:88.6%		 Coverage:88.3%

Colour analysis

Figure 6.35 shows the percentage changes in L^* and a^* for fabrics gauged in 40 °C wash solutions. Again, it can be seen that removal is higher when twice the CMC of the surfactant is used. It can also be seen that at this concentration removal from the underside is higher than from the topside, but for all other conditions removal is higher from the topside. The surfactant is aiding transport of the sebum through the fabric by solubilising it in the wash solution. Without this mechanism the sebum on the underside is not able to move through the pores and hence is not removed. Removal of sebum when water or 0.1 times the CMC of the surfactant are used is very similar, therefore the surfactant at low concentration is not giving any benefit over water alone. This suggests a concentration of surfactant above the CMC is required to aid removal, particularly from the underside of the fabric.

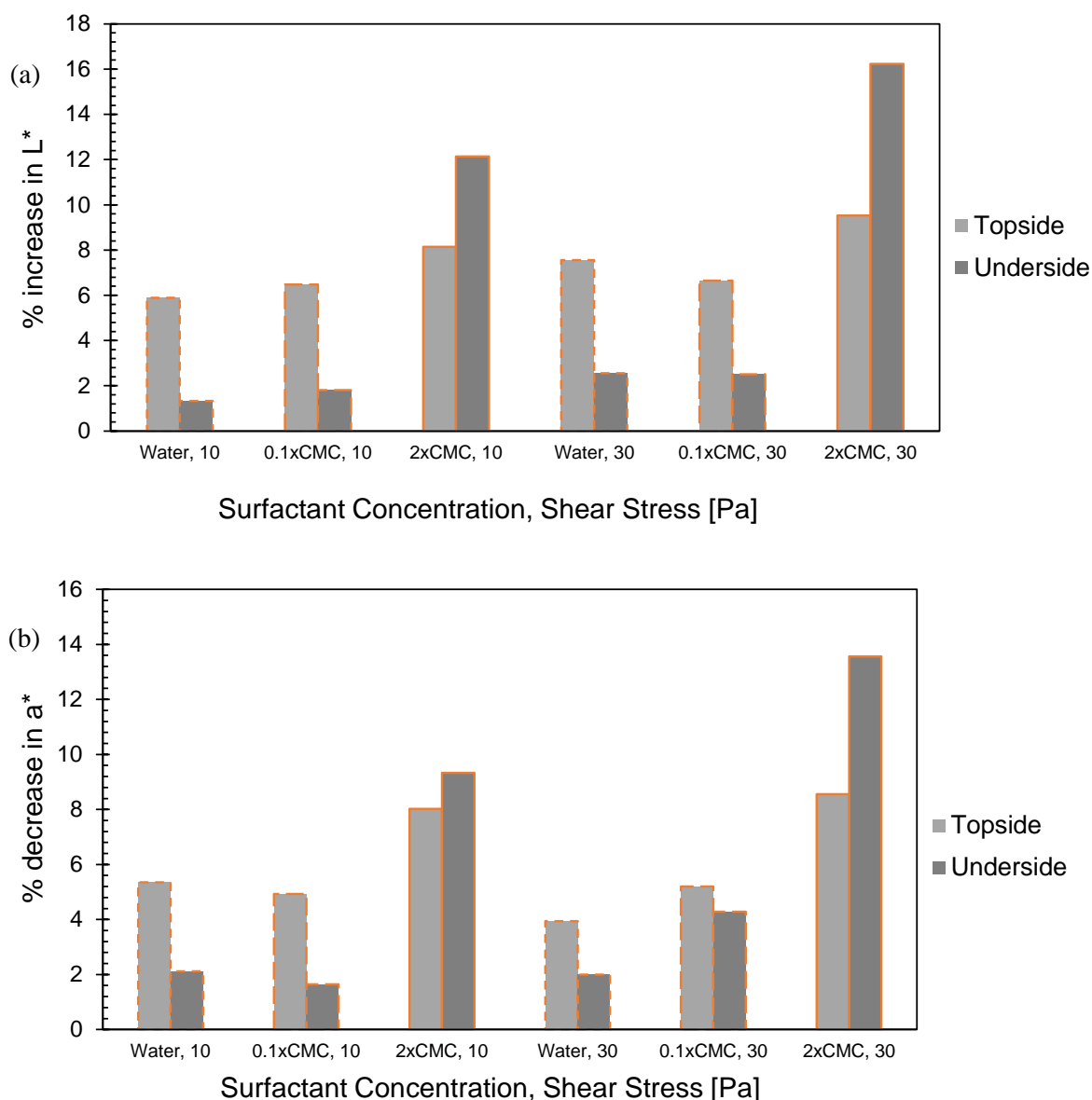





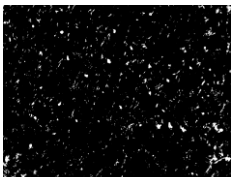
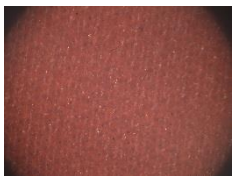



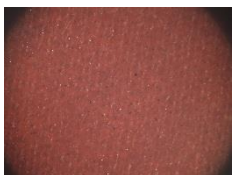


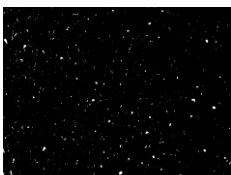
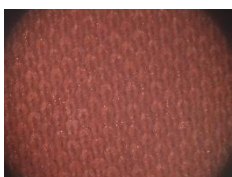
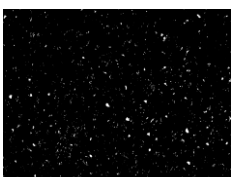
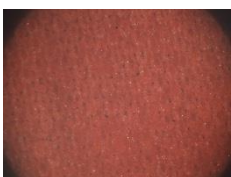

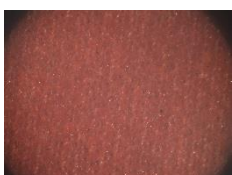
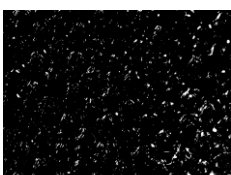
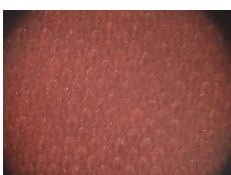
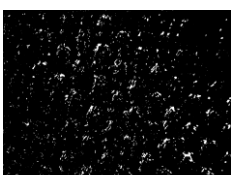


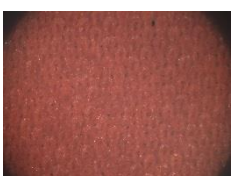
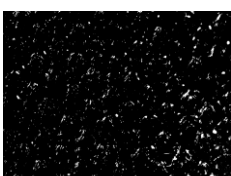
Figure 6.35. (a) ΔL^* and (b) Δa^* values for the top and underside of fabrics gauged in surfactant solution at 40 °C with 10 Pa and 30 Pa. Water, 0.1 x CMC and 2 x CMC wash solutions were tested.






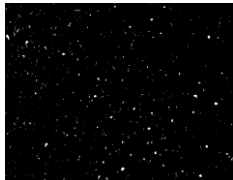

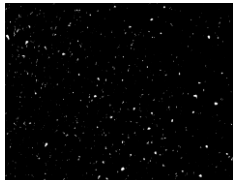




6.2.2.3. Effect of surfactant concentration at 20 °C

Microscope images

Table 6.5 shows microscope images processed with ImageJ. It can be seen that there are no differences between any samples at 20 °C, indicating that at this temperature the sebum is still a waxy solid and hence removal is not possible with the gauge at these shear stresses. It is likely that more removal may be possible if higher shear stresses could be achieved.

Table 6.5. Microscope images of gauged polyester at 20 °C with water and surfactant at a concentration of 0.1 x and 2 x CMC.

	Topside Image	Topside ImageJ	Underside Image	Underside ImageJ
20 °C Water Soaked		 Coverage: 98.4%		 Coverage: 96.2%
20 °C Water 10 Pa		 Coverage: 99.3%		 Coverage: 98.2%
20 °C Water 30 Pa		 Coverage: 98.5%		 Coverage: 98.7%
20 °C 0.1 x CMC Soaked		 Coverage: 98.4%		 Coverage: 98.9%
20 °C 0.1 x CMC 10 Pa		 Coverage: 96.3%		 Coverage: 96.3%
20 °C 0.1 x CMC 30 Pa		 Coverage: 98.2%		 Coverage: 96.4%

20 °C 2 x CMC Soaked		 Coverage: 98.9%		 Coverage: 98.5%
20 °C 2 x CMC 10 Pa		 Coverage: 99.0%		 Coverage: 98.7%
20 °C 2 x CMC 30 Pa		 Coverage: 98.5%		 Coverage: 98.1%

Colour analysis

L* and a* results, presented in Figure 6.36, show the change in colour when fabrics in 20 °C wash solution are gauged at two different shear stresses. It can be seen that removal is much higher from the topside than the underside. Again, this is due to the state of the sebum at this temperature, which is more solid. Without being molten the surfactant cannot penetrate the soil and therefore removal is much more difficult. The sebum on the underside is therefore unable to travel through the pores to be removed by the gauge on the top surface. A small amount of removal is seen on the topside, therefore the gauge must be removing a small amount of this soil. A slight increase in removal is seen when twice the CMC of the surfactant is used, showing the surfactant must aid removal from this surface. No significant difference is seen between water and 0.1 times the CMC, showing the importance of concentration of the surfactant.

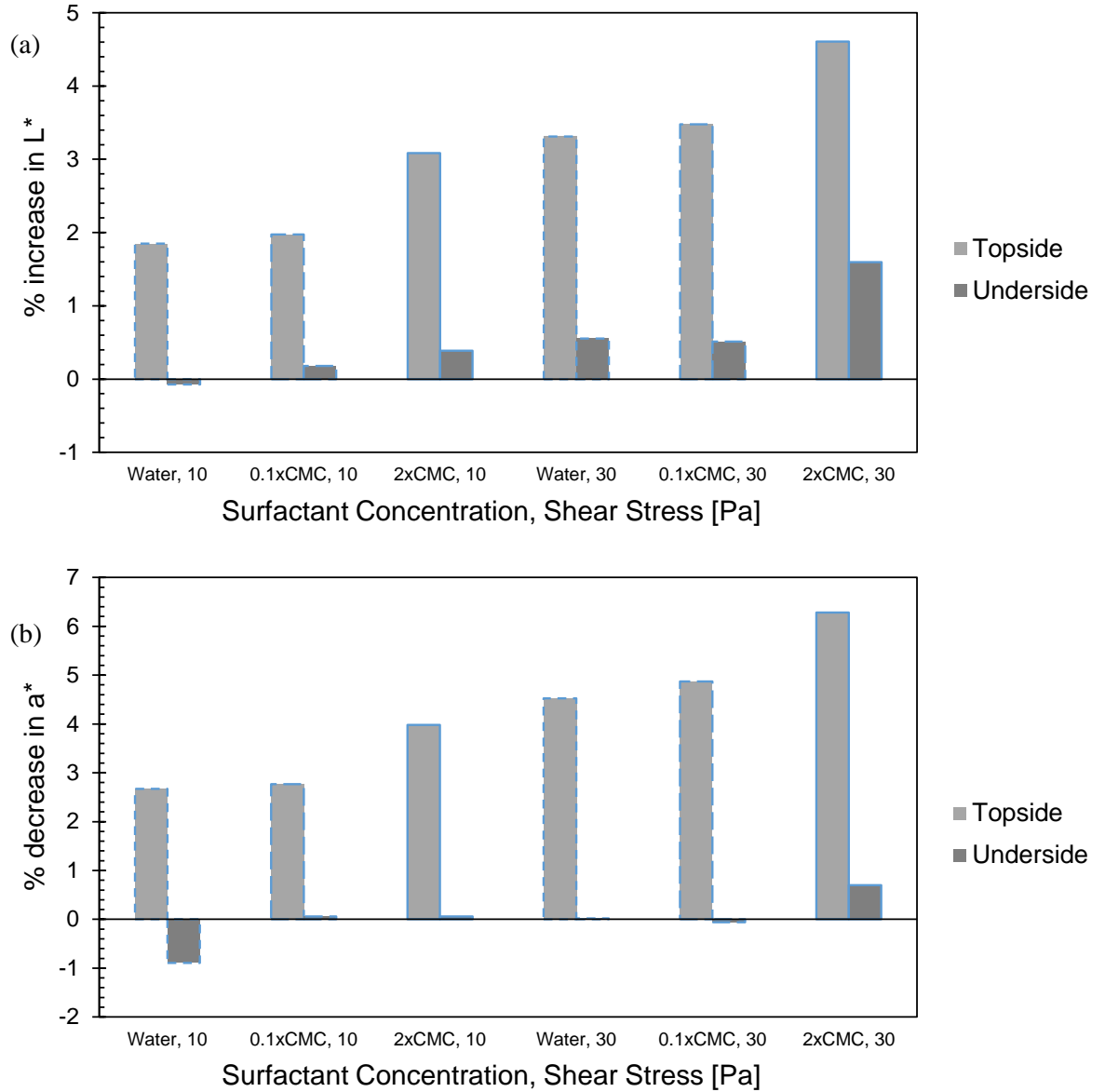


Figure 6.36. (a) ΔL^* and (b) Δa^* values for the top and underside of fabrics gauged in surfactant solution at 20 °C with 10 Pa and 30 Pa. Water, 0.1 x CMC and 2 x CMC wash solutions were tested.

6.2.2.4. Effect of nozzle geometry

Two additional nozzles were tested with geometries shown in Figure 2.12 with $\beta = 5^\circ$ and $\beta = 15^\circ$ which maximised shear stress and normal force, respectively. These experiments were performed at 60 °C with twice the CMC of surfactant at 30 Pa shear stress as removal was highest with the traditional nozzle shape under these conditions. Figure 6.37 shows the footprint of these nozzles on the soiled polyester fabric. This matches the FDG profiles presented in Figures 2.12 and 2.13, which

highlight the areas where normal force and shear stress are maximised. It can be seen that removal is higher when the nozzle has a 5° angle, but removal covers a much smaller area than for the traditional nozzle shown above in Figure 6.33.

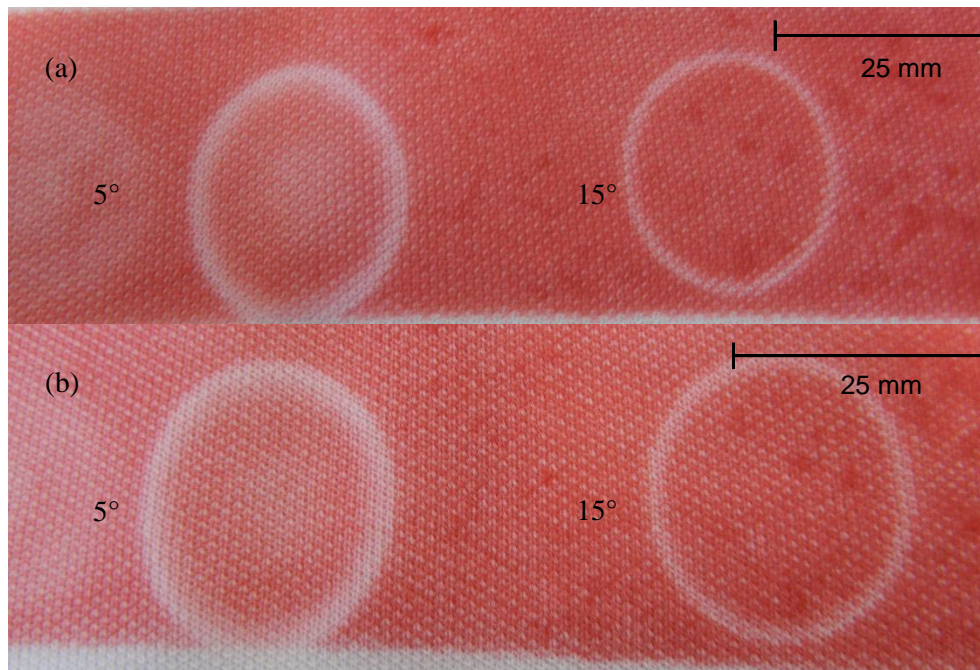

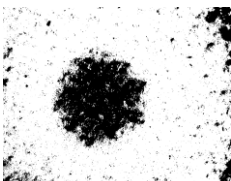
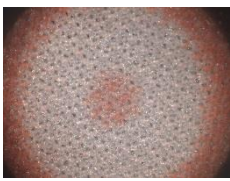
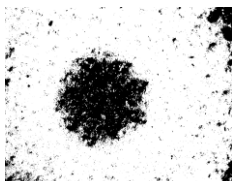

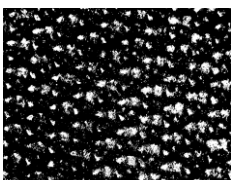

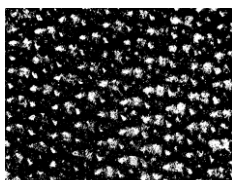

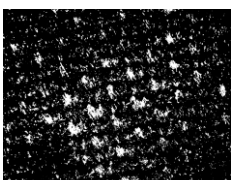

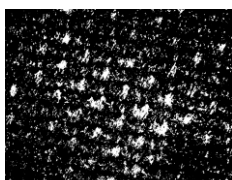


Figure 6.37. Images of gauged area of fabrics showing (a) topside and (b) underside of fabrics in 60°C surfactant solution at $2 \times \text{CMC}$ for two different nozzles.

Microscope images

Microscope images of the gauged areas using three nozzle geometries are presented in Table 6.6. It can be seen that the traditional nozzle gives much more removal over a wider area. There is some difference between the two new geometries, with the 5° nozzle giving slightly higher removal. This nozzle was predicted to maximise shear stress therefore increased removal could be expected. The high shear stress is concentrated around the edge of the nozzle so removal from the centre of the footprint is lower than the traditional nozzle.

Table 6.6. Microscope images of gauged polyester at 60 °C with 2 x CMC using 3 nozzles with different geometries.

	Topside Image	Topside ImageJ	Underside Image	Underside ImageJ
Traditional nozzle		 Coverage:18.1%		 Coverage:17.7%:
5° nozzle		 Coverage: 82.9%		 Coverage: 82.7%
15° nozzle		 Coverage: 88.3%		 Coverage: 86.3%

Colour analysis

L* and a* results, presented in Figure 6.38, show the same trend as the microscope images. It can be seen that removal is much higher using the traditional nozzle, and the least removal is seen when the 15° nozzle is used. These results show more of a difference between the 5° and 15° nozzles, which is to be expected as the microscope images are thresholded so any area above a certain level of redness is selected, whereas the spectrophotometer determines the average colour of the entire gauged area. Removal is equal from the topside and underside as the trend seen previously with polycotton in section 6.2.1. This may be because, at 60 °C, when the soil has loosened from the fabric by the force of the gauge it is more likely to remain in the surfactant solution rather than reattaching to the top surface of the fabric.

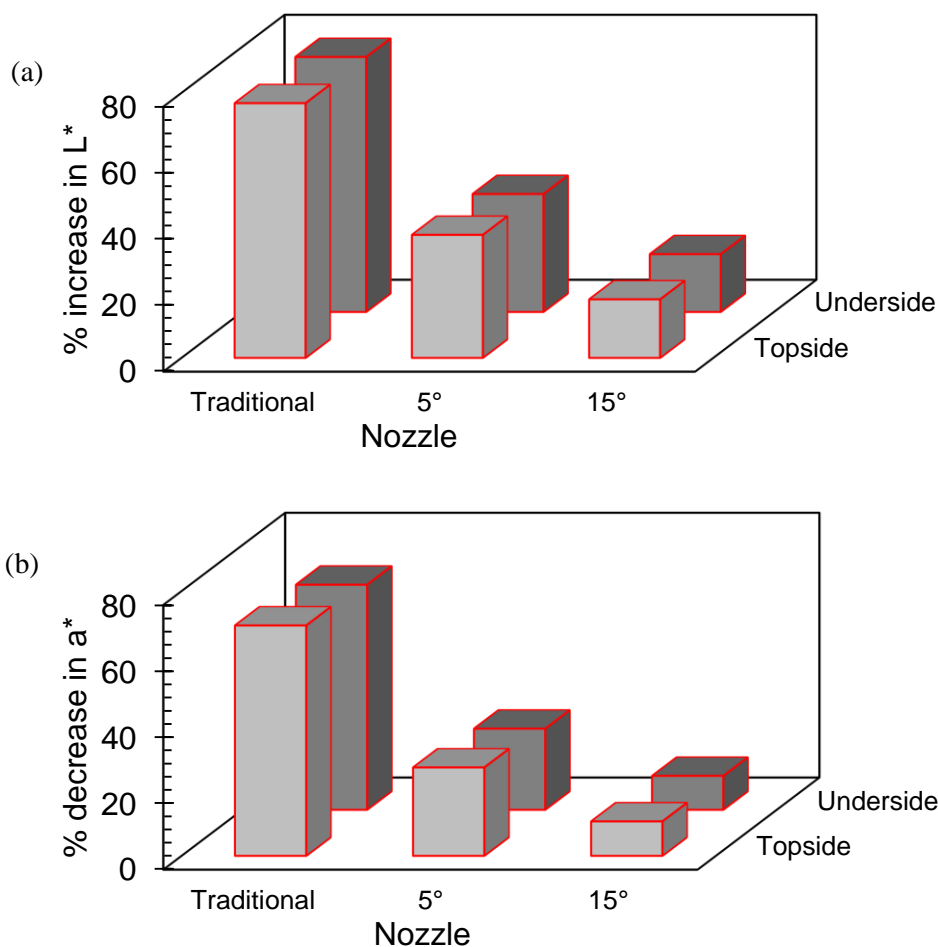


Figure 6.38. (a) ΔL^* and (b) Δa^* values for the top and underside of fabrics gauged in 2 x CMC surfactant solution at 60 °C with 30 Pa shear stress using 3 different nozzle geometries.

6.2.3. Cotton

The same experiment was to be repeated on cotton using the gear pump and flow meter set up to generate a constant mass flow. Again, a flow rate of 500 mL.min⁻¹ was tested. It was found that even with three weights hanging from the fabric, with a total mass of 1125 g, the virgin fabric lifted up towards the gauge. A flow rate of 100 mL.min⁻¹ was tested and calibrations were possible at this flow rate. When the soiled fabric was then tested it was found that this also moved up towards the gauge at the lower flow rate, which is thought to be because the sebum prevented flow through the fabric as resistance of soiled cotton is very high. Since the fabric is stretchy, when it is exposed to a high enough force from the nozzle it is sucked upwards invalidating the experiment.

To enable soiled cotton to be analysed with the FDG a new experimental set up would be required that tensioned the fabric further. One possible solution would be to construct a platform to tension the fabric with a tensioning roller similar to the ones retrofitted onto the rubbing and stretching rigs. This would prevent the fabric moving when the nozzle approaches the surface.

6.2.4. Discussion on FDG

Both polycotton and polyester showed that the gauge is able to pull the sebum through the pores of the fabric, removing it from the underside of the fabric and depositing some sebum on the top side. This indicates the sebum is able to move through the pores and reposition itself on another area of the fabric, an effect which has not been isolated elsewhere in this thesis. As would be expected, the magnitude of this effect is proportional to the shear stress applied. This is an effect that has not been seen previously with FDG, for example when used on metal plates or membranes, and shows the potential of FDG for investigations with fabric. This is due to the fact that the fabric has larger pores. It can be seen that temperature has the greatest effect when used in conjunction with FDG, due to the fact that the sebum is fully liquefied at 60 °C so both movement through the pores and removal from the surface will be greatly assisted. The addition of surfactant is seen to also aid removal, particularly from the underside of the fabric, so the surfactant is helping movement of the surfactant on the fibre surface, but is less effective at aiding removal from the top surface. Two additional nozzles were also tested, which maximised either shear stress or normal force.

Some limitations have been found, including the difficulties with sufficiently tensioning the fabric. It is suspected that tensioning the fabric will cause some removal, but that this removal will be significantly less than the removal caused by the gauge. This could be overcome by designing a tensioning platform with a similar set up to the tensioning wheel used on the rubbing and stretching rigs. Currently, testing has only been completed when the fabric has been stretched over a metal platform. It would be interesting to extend this testing to include fabric without a support underneath. Again this would require a better way of tensioning the fabric.

Chapter 7: Effect of Mechanical Action

This chapter investigates the effect of mechanical actions in the form of rubbing and stretching on the cleaning of cotton and polyester soiled with sebum at different temperatures and different surfactant concentrations.

7.1. Rubbing

For rubbing experiments a downward force of 14.35 N created by two parallel springs was moved horizontally over the fabric stretched over a platform. Each experiment rubbed the full length of the fabric 100 times over ten minutes.

7.1.1 Polyester

7.1.1.1. Effect of Temperature

Mass, colour and resistance measurements

Figure 7.1 shows the mass loss after rubbing at all three temperatures is high, with removal above 70% even at 20 °C. Removal as judged by resistance is also very high. Colour change is less than both of these, which may be due to some of the dye remaining on the fabric. Removal is thought to be high as the rubbing blade creates a downward force on the fabric pushing the sebum off the surface, but this force will also manipulate the pores changing their shape. If the pores are stretched this will loosen sebum in the pores, and if the pore is compressed, sebum in the pore will be forced to move to the surface where it will be removed. This effect will be greater due to the elasticity of the fabric allowing greater manipulation.

As with other cleaning methods, the removal of sebum increases with increasing temperature. When all four measures are considered it can be concluded that the additional removal caused by rubbing

compared to soaking alone is approximately the same for all three temperatures, so there does not appear to be a synergistic effect between rubbing and increased temperature.

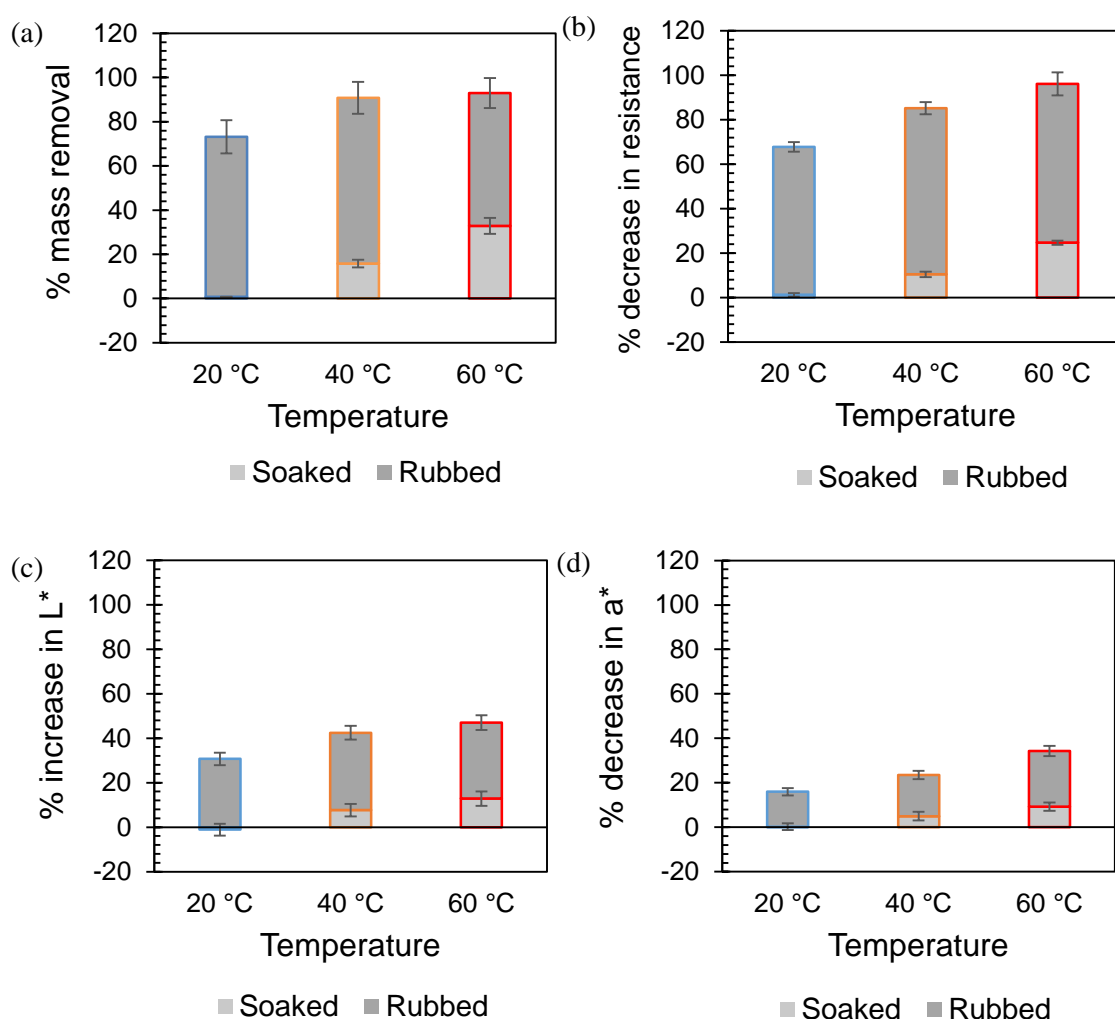


Figure 7.1. Effect of temperature on rubbing of polyester soiled with sebum. Surfactant was used at a concentration of 2 x CMC. Cleaning is measured by (a) % mass removal, (b) % decrease in resistance, (c) % increase in L^* and (d) % decrease in a^* . The error bars represent \pm one standard deviation for three fabrics. Five measurements were taken from each fabric for colour and resistance.

Colour of top and underside of fabric

It was suspected that removal may be greater from the side of the fabric subject to rubbing, however interestingly, removal from the top and underside of the fabric appears to be very similar, as shown in Figure 7.2. This may be because the underside of the fabric is also subject to the same force as the topside therefore sebum is still removed.

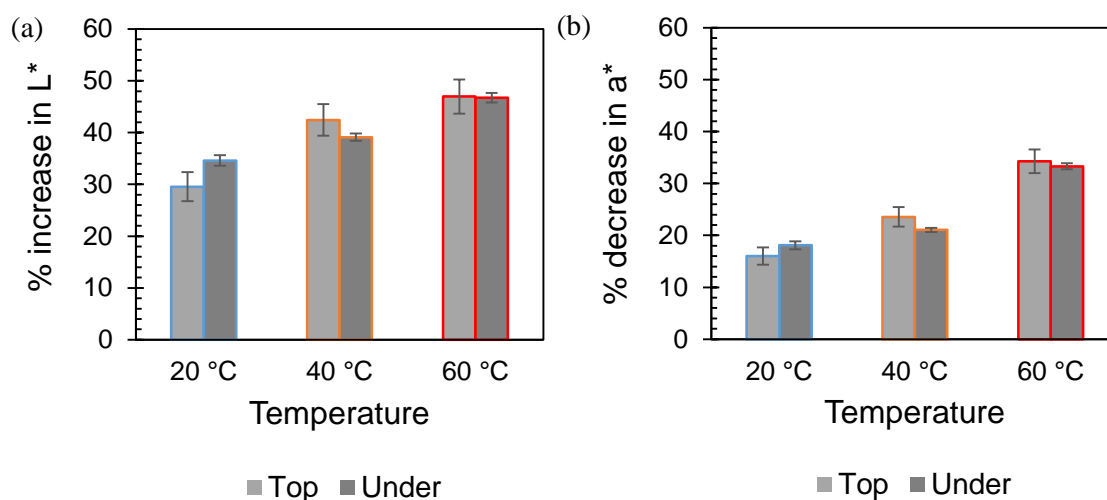


Figure 7.2. Comparison of the colour of the top and underside of polyester soiled with sebum cleaned using the rubbing rig at 20 °C, 40 °C and 60 °C with surfactant at a concentration of 2 x CMC. Colour is measured as (a) L^* and (b) a^* . The error bars represent \pm one standard deviation for three fabrics. Five measurements were taken from each fabric.

Mass per unit area

Figure 7.3 shows the mass per unit area of the polyester fabrics after cleaning by rubbing at the three temperatures. In contrast to other results presented previously, the mass of the clean fabric surrounding the soiled area has significantly decreased after rubbing. This is likely to be because rubbing has stretched the fabric giving less mass per unit area after testing. For all three temperatures the soiled area has significantly decreased in mass, however it is only for the central strip at 60 °C that the mass is on par with the cleaned area of the fabric. The central strip of the fabric may have been better cleaned as when sebum was removed here by the downward force of the rubbing blade it may have pushed it out to the adjacent soiled strips, especially since the mass in the centre was slightly higher to begin with. Mass loss is then in line with temperature as expected.

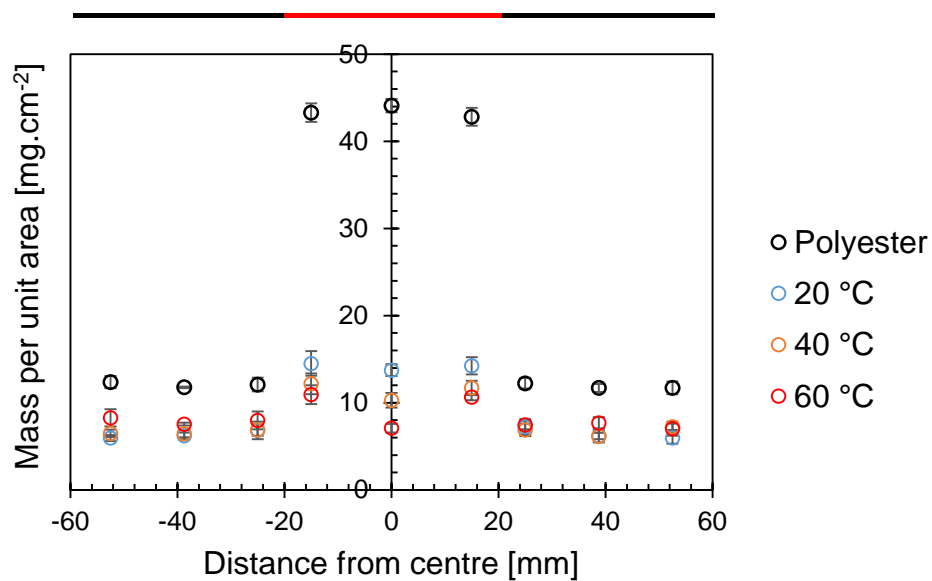


Figure 7.3. Mass per unit area of polyester soiled with sebum cleaned using the rubbing rig at 20 °C, 40 °C and 60 °C with surfactant at a concentration of 2 x CMC. The error bars represent \pm one standard deviation for three fabrics.

FTIR

In the FTIR spectra in Figure 7.4 it can be seen that the sebum peaks have been reduced in all of the samples, and to a greater extent at increased temperature in line with mass results. Polyester peaks that were masked on the soiled polyester spectrum are visible at all three temperatures, for example the peaks at 1240 and 1090 cm^{-1} . FTIR results support mass loss results.

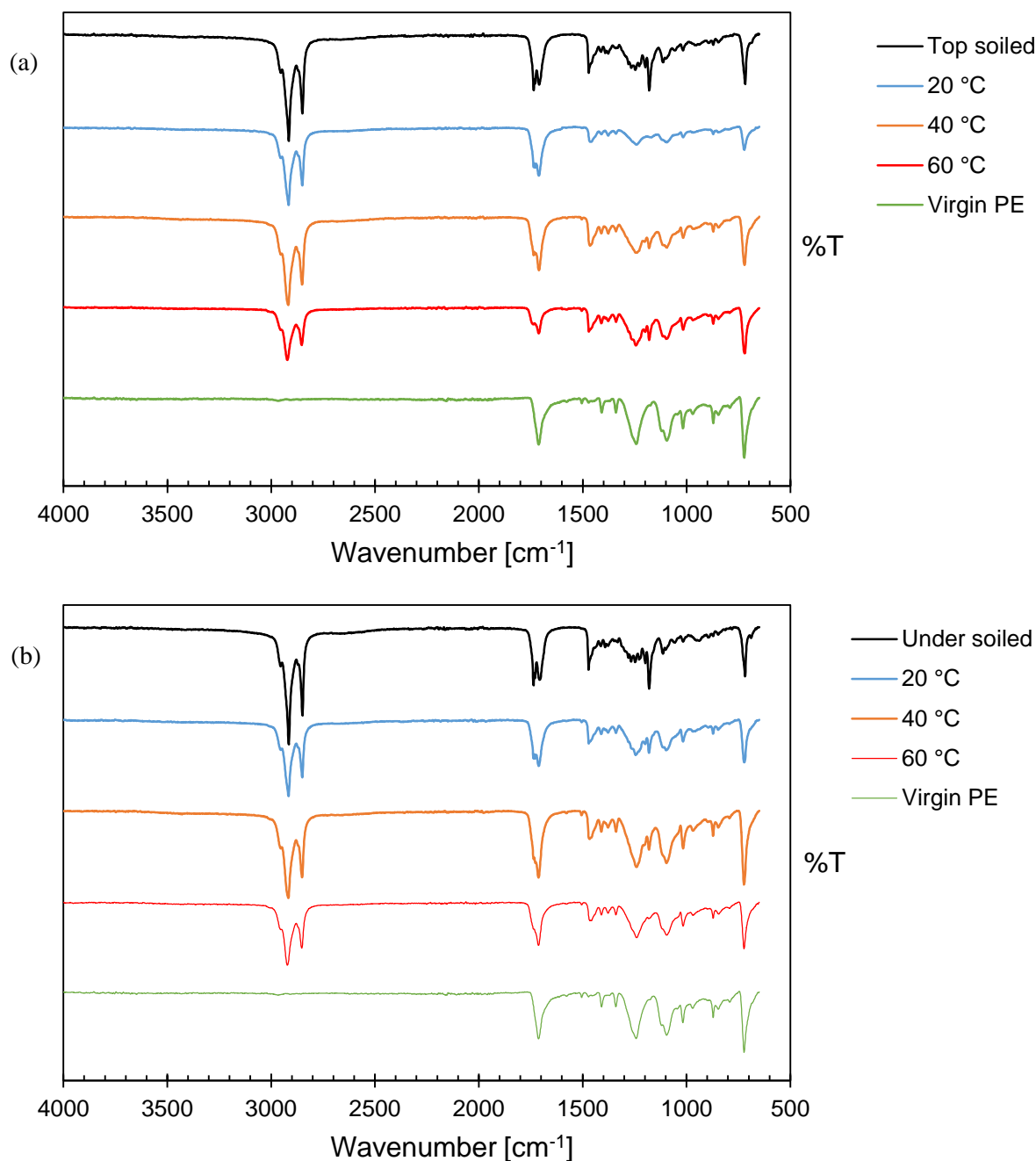


Figure 7.4. FTIR of polyester soiled with sebum cleaned using the rubbing rig at 20 °C, 40 °C and 60 °C with surfactant at a concentration of 2 x CMC. This is compared to soiled and virgin polyester for both the (a) top and (b) underside of the fabric.

Zeta Potential

Interestingly, rather than occupying the space between the virgin and soiled polyester, the rubbed samples have a zeta potential more negative than virgin polyester, as shown in Figure 7.5. There are a number of possible explanations for this. Firstly, the rubbing may lead to selective removal of the

constituents of sebum, however this seems unlikely when the FTIR is considered. Secondly, the mechanical action may have damaged the polyester surface exposing new polyester material. It is thought that the polyester has been modified with a sizing agent, so the action of rubbing may have removed this giving the polyester different electrochemical properties. The differences observed by the different temperatures are minimal.

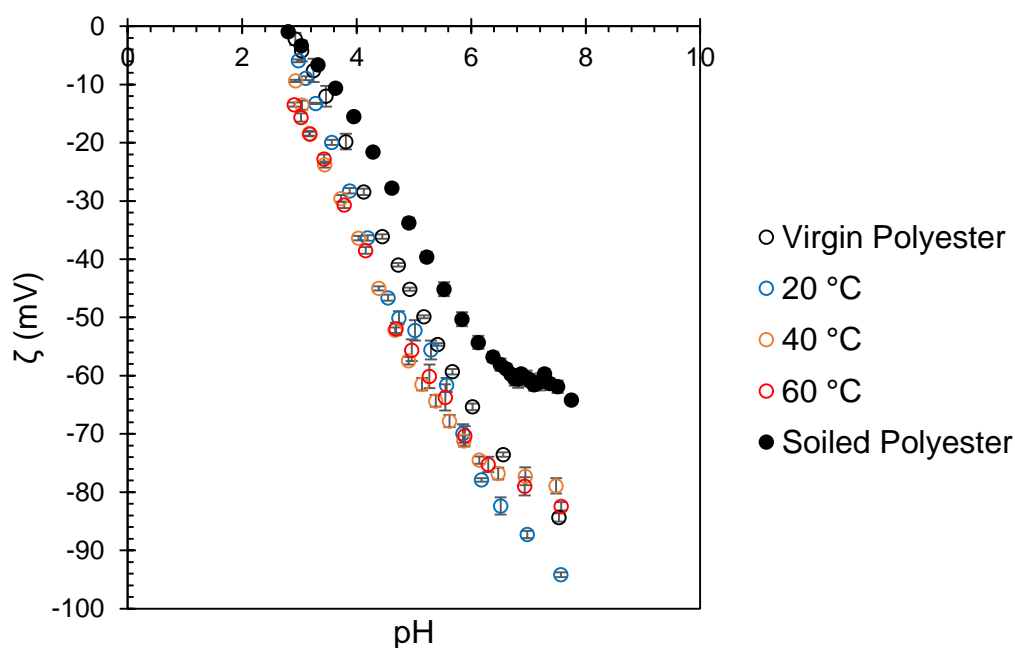


Figure 7.5. Effect of temperature on zeta potential for polyester soiled with sebum and rubbed at 20 °C, 40 °C and 60 °C with surfactant at a concentration of 2 x CMC. The error bars represent \pm one standard deviation for four repeat measurements taken on each fabric.

SEM

SEM images were taken for polyester rubbed at 20 °C and 60 °C with 2 x CMC. Fabrics washed at 20 °C have more soil on the fibres then those washed at 60 °C, as seen on Figure 7.6 at x500 magnification. The biggest difference appears to be in the gaps between fibres, where at 20 °C we see some sebum bridging between fibres, whereas sebum washed at 60 °C is found on the individual fibres. The differences are much less noticeable on the x20 and x100 images. In terms of the overall structure of the fabric, no difference can be seen at either temperature compared to soiled polyester, Figure 4.21, indicating that rubbing does not change the structure of the fabric.

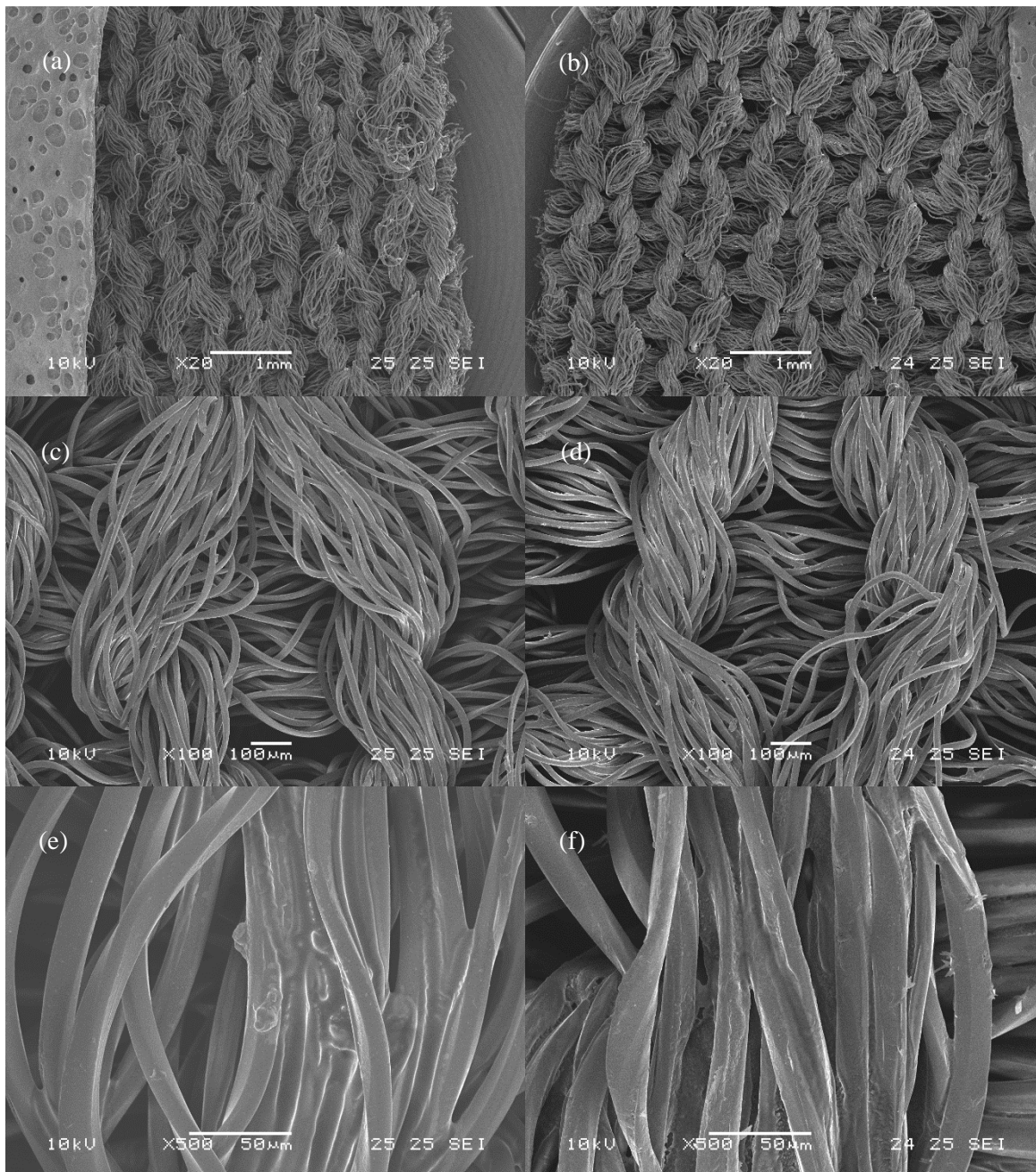


Figure 7.6. SEM images of soiled polyester rubbed with 2 x CMC surfactant solution at (a, c, e) 20 °C and (b, d, f) 60 °C at (a, b) x20 (c, d) x100 and (e, f) x500 magnifications.

7.1.1.2. Effect of surfactant concentration at 40 °C

Mass, colour and resistance measurements

Mass, colour and resistance data for polyester rubbed in 40 °C wash solution is given in Figure 7.7.

It can be seen that the best level of cleaning is achieved with twice the CMC of the surfactant,

although 0.1 times the CMC gives a benefit over using water alone. This is interesting as it is often thought that higher levels of surfactant, above the CMC, are needed to show a cleaning benefit. This indicates there is some synergistic effect when rubbed is combined with chemical action. A similar effect was observed by Han et al. (2015), when experiments performed in a Terg-O-Tometer showed a synergistic effect between detergent concentration and agitation. In this case, the surfactant may loosen the sebum, allowing easy removal by the rubbing blade.

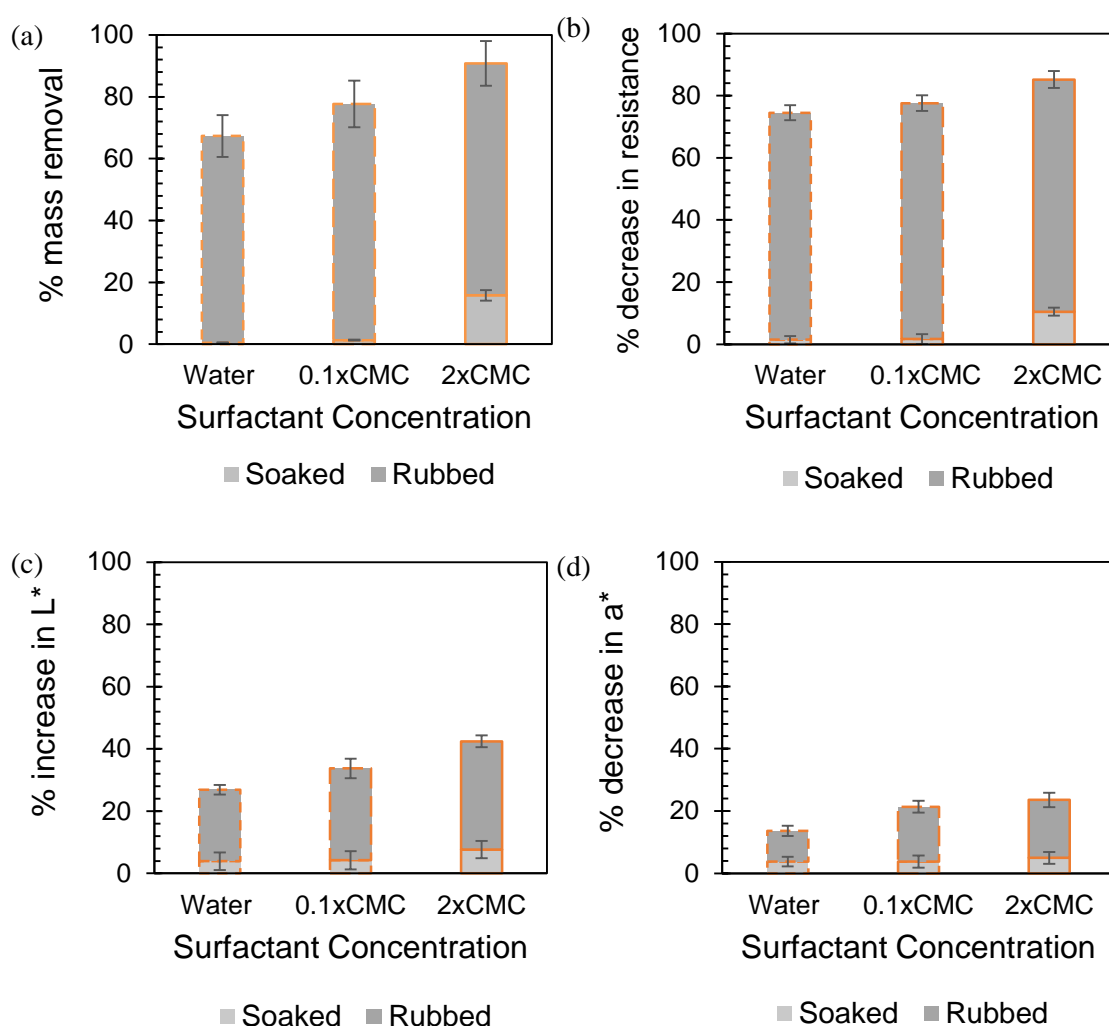


Figure 7.7. Effect of surfactant concentration on rubbing at 40 °C for polyester soiled with sebum. Cleaning is measured by (a) % mass removal, (b) % decrease in resistance, (c) % increase in L^* and (d) % decrease in a^* . The error bars represent \pm one standard deviation for three fabrics. Five measurements were taken from each fabric for colour and resistance.

Colour of top and underside of fabric

Figure 7.8 shows that the colour of the underside follows the same trend as the colour of the topside, with removal increasing as surfactant concentration is increased. It can also be seen that the removal from the underside of the fabric is less than the removal from the topside. This is likely to be because the rubbing action is on the topside of the fabric.

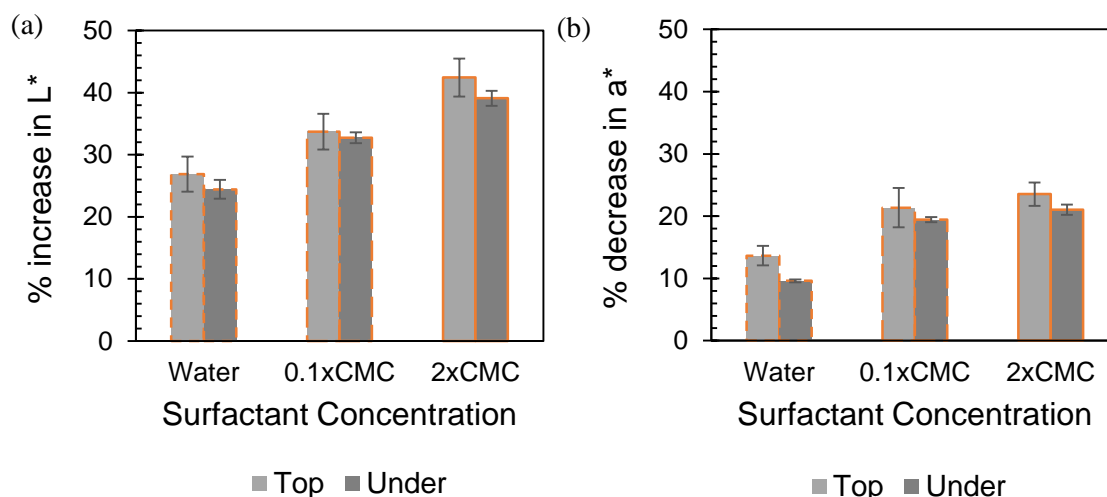


Figure 7.8. Comparison of the colour of the top and underside of polyester soiled with sebum cleaned using the rubbing rig at 40 °C with water and surfactant at a concentration of 0.1 x and 2 x CMC. Colour is measured as (a) L* and (b) a*. The error bars represent \pm one standard deviation for three fabrics. Five measurements were taken from each fabric.

Mass per unit area

Mass per unit area measurements for the three wash conditions are given in Figure 7.9. It can be seen that the mass of the clean area has decreased, which is due to stretching of the fabric caused by the elasticity of the polyester fibres. The mass of the soiled area has decreased in line with mass removal data presented previously. Water shows the least removal, with more removal as surfactant concentration is increased.

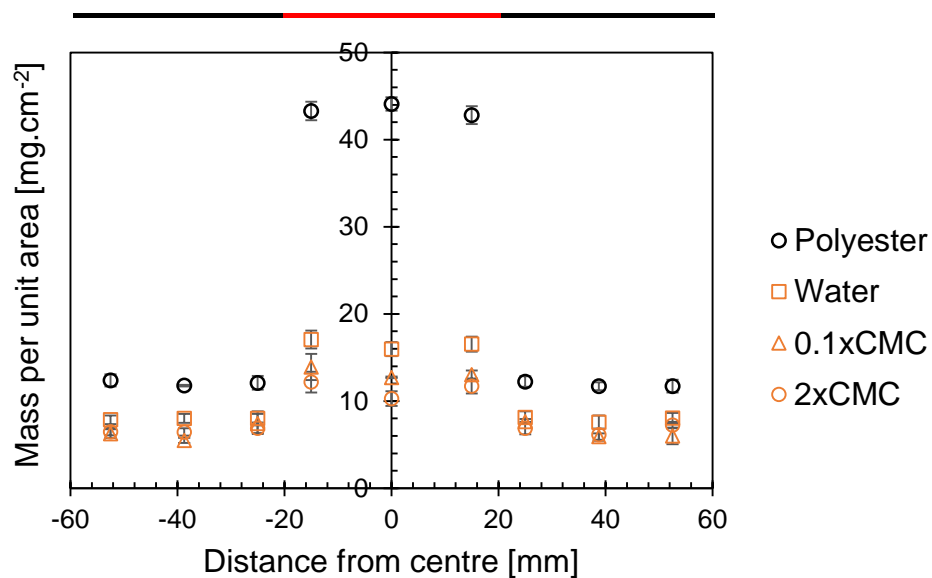


Figure 7.9. Mass per unit area of polyester soiled with sebum cleaned using the rubbing rig at 40 °C with water and surfactant at a concentration of 0.1 x and 2 x CMC. The error bars represent \pm one standard deviation for three fabrics.

FTIR

Figure 7.10 shows the FTIR for the polyester rubbed in the three wash solutions. Although sebum peaks at 2920 and 2850 cm^{-1} are visible on all three samples, the polyester peaks at 1240 and 1090 cm^{-1} become more visible as the surfactant concentration is increased on both the topside and underside of the fabric. This indicates higher removal, although there are not huge differences between the three samples, in line with previous results.

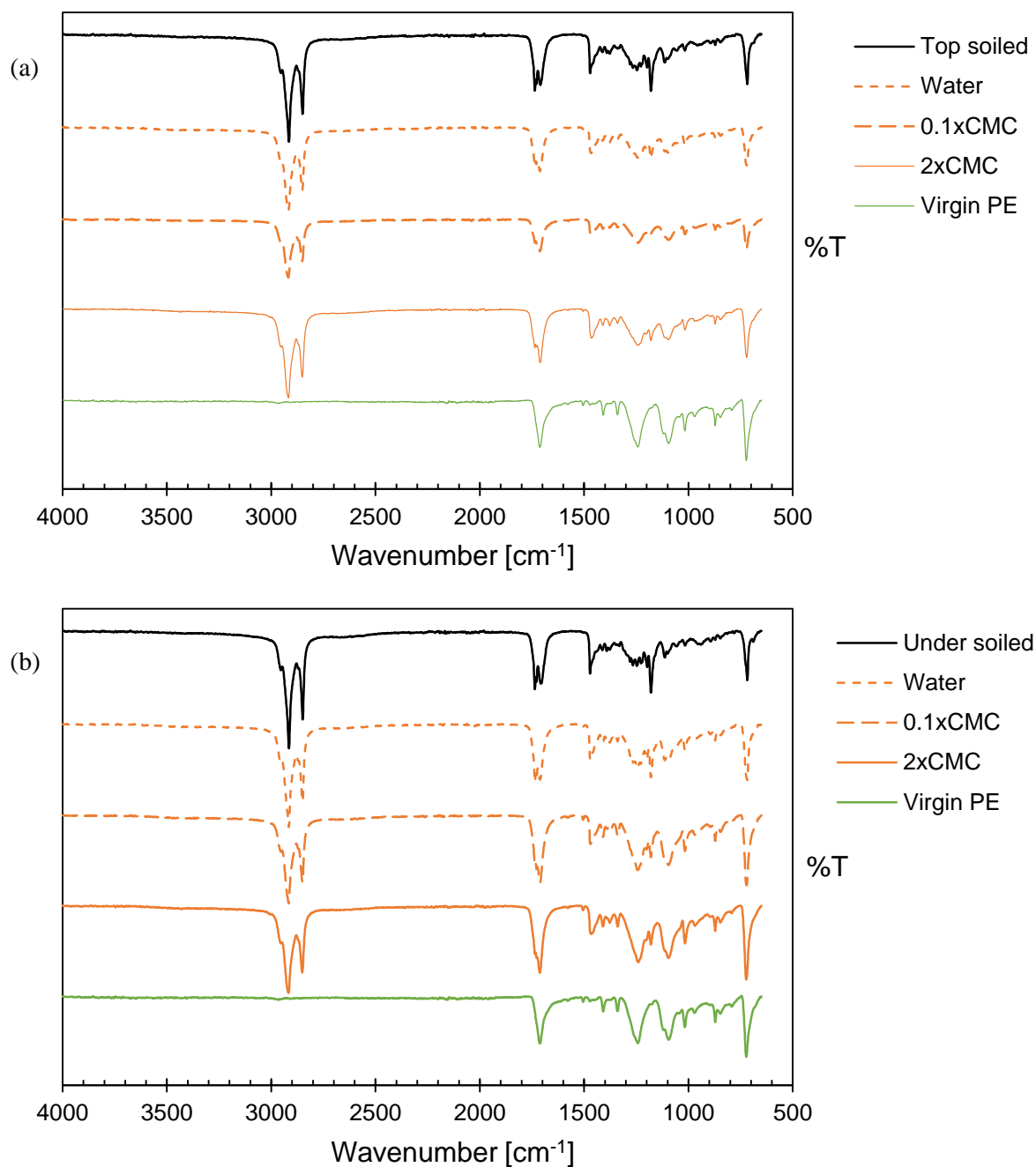


Figure 7.10. FTIR of polyester soiled with sebum cleaned using the rubbing rig at 20 °C with water and surfactant at a concentration of 0.1 x and 2 x CMC. This is compared to soiled and virgin polyester for both the (a) top and (b) underside of the fabric.

Zeta Potential

Zeta potential at the different surfactant concentrations, presented in Figure 7.11, show the same trend found in Figure 7.5. Rather than giving a zeta potential somewhere between the soiled and

virgin polyester as expected, the zeta potential is instead more negative than virgin polyester. There is very little difference between the three surfactant concentrations.

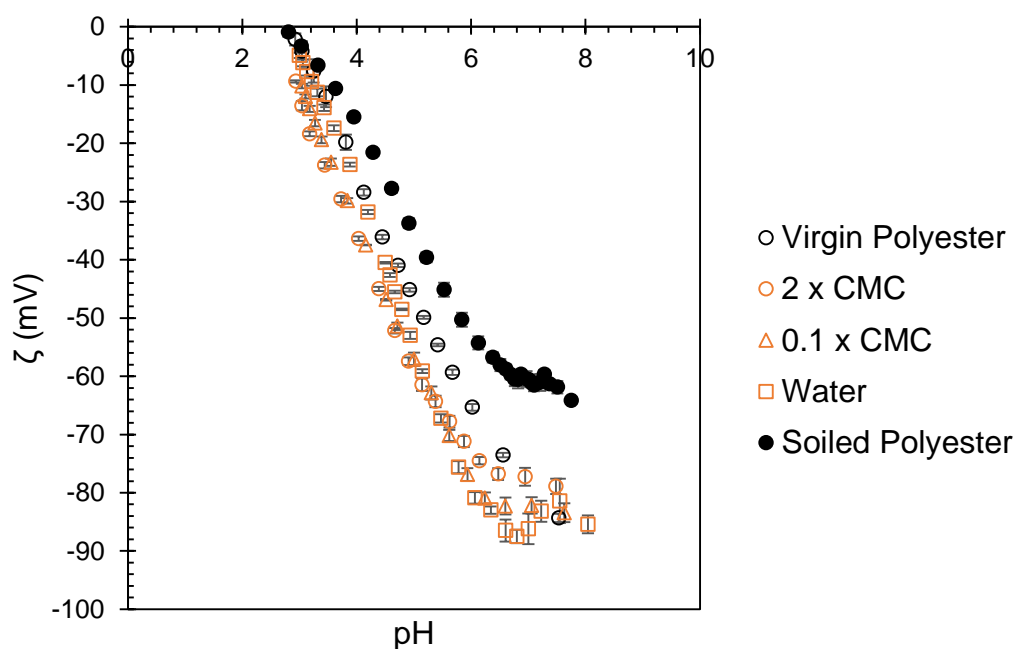


Figure 7.11. Effect of surfactant concentration on zeta potential for polyester soiled with sebum and rubbed at 40 °C with surfactant solution at 0.1 x CMC and 2 x CMC as well as water. The error bars represent \pm one standard deviation for four repeat measurements taken on each fabric.

To investigate whether this change is due to the wash conditions or the action of rubbing virgin polyester was also rubbed and its zeta potential measured, as shown in Figure 7.12. Rubbing virgin polyester also shifts results to a more negative zeta potential, therefore the change observed above with rubbed soiled polyester must be a change in the polyester itself. It is likely that the action of rubbing is removing a sizing agent on the polyester, exposing the polyester fibre that had initially been coated, or damaging the polyester fibre.

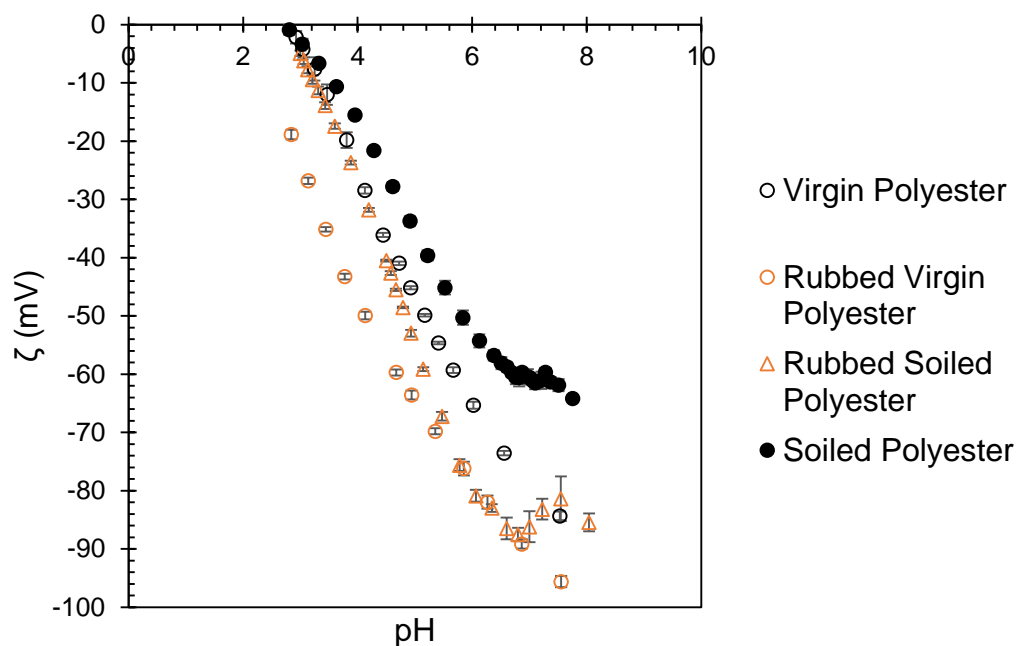


Figure 7.12. Comparing the zeta potential of virgin and soiled polyester fabrics rubbed in 40 °C water. The error bars represent \pm one standard deviation for four repeat measurements taken on each fabric.

The FTIR spectrum of virgin polyester that had been rubbed in 40 °C water was also tested to investigate whether the rubbing action has changed the chemical makeup of the polyester surface. Figure 7.13 shows no difference between virgin polyester and virgin rubbed polyester therefore the change in zeta potential found above is not due to a change in the chemical makeup of the surface found by FTIR.

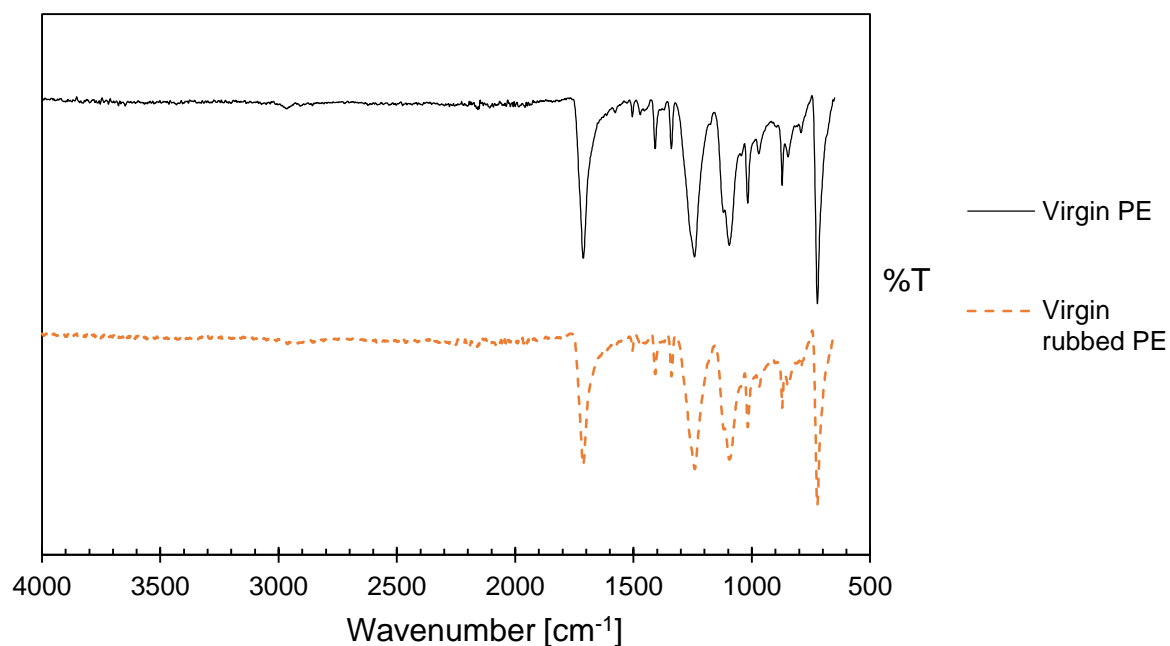


Figure 7.13. FTIR of virgin polyester rubbed in at water at 40 °C compared to virgin polyester.

7.1.1.3. Effect of surfactant concentration at 20 °C

Mass, colour and resistance measurements

Removal is less at 20 °C than has been seen at 40 °C, as shown in Figure 7.14. This is likely to be because sebum is molten at 40 °C, so will be more easily removed by the rubbing action. When colour is used to analyse cleaning, removal is fairly similar for all three concentrations of surfactant. This shows that removal is driven mainly by rubbing action rather than the level of surfactant. However, water gives significantly lower removal than when surfactant is used in terms of mass and resistance. This suggests that the sebum is removed from the surface but surfactant is required to remove sebum from the pores at this temperature.

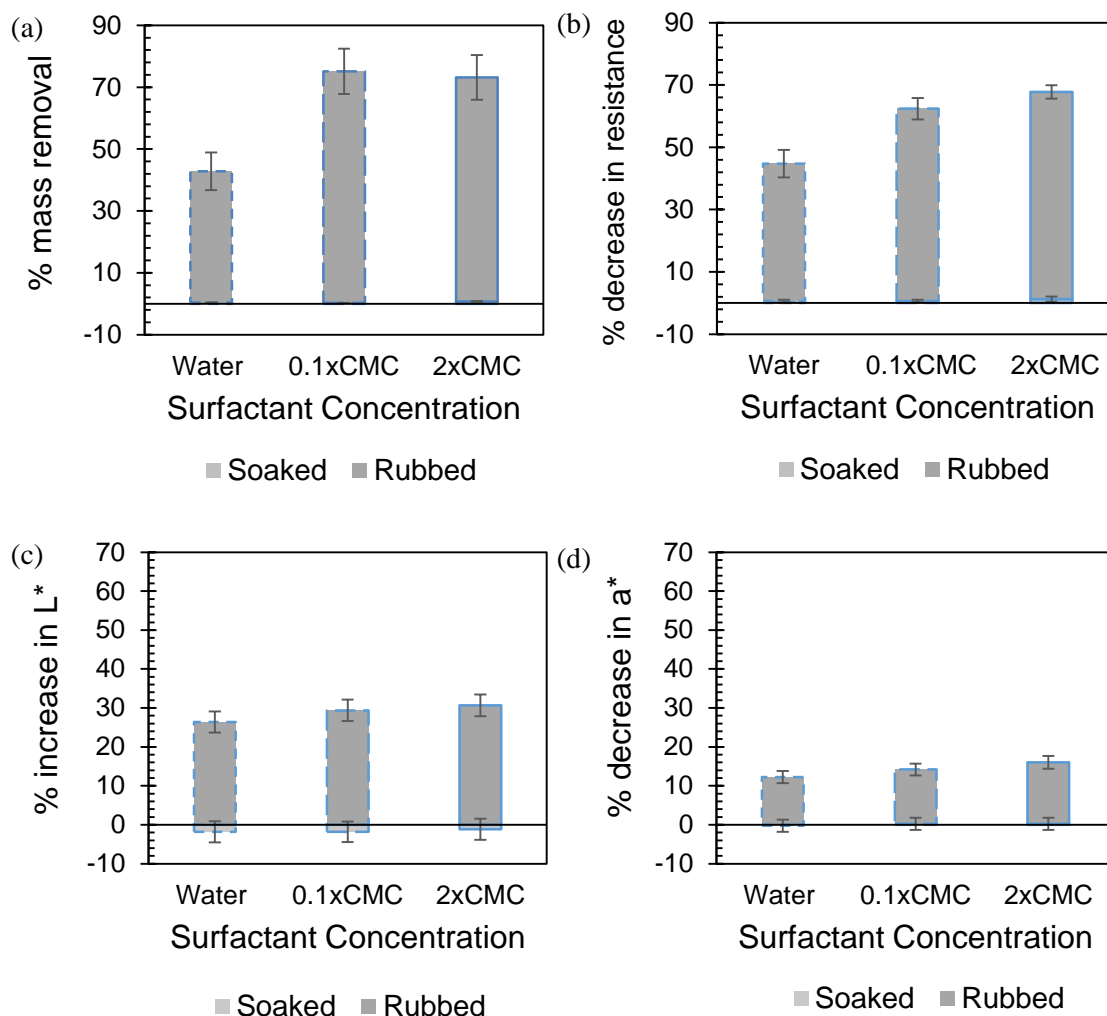


Figure 7.14. Effect of surfactant concentration on rubbing at 20 °C for polyester soiled with sebum. Cleaning is measured by (a) % mass removal, (b) % decrease in resistance, (c) % increase in L^* and (d) % decrease in a^* . The error bars represent \pm one standard deviation for three fabrics. Five measurements were taken from each fabric for colour and resistance.

Colour of top and underside of fabric

Figure 7.15 shows the colours of the topside and underside of fabrics rubbed in 20 °C wash solution. For the two solutions containing surfactant removal from the underside of the fabric is actually higher than removal from the topside of the fabric. This is not the case for water, which may be explained by the fact that less mass has been removed and resistance data suggests that sebum has not been removed from the pores.

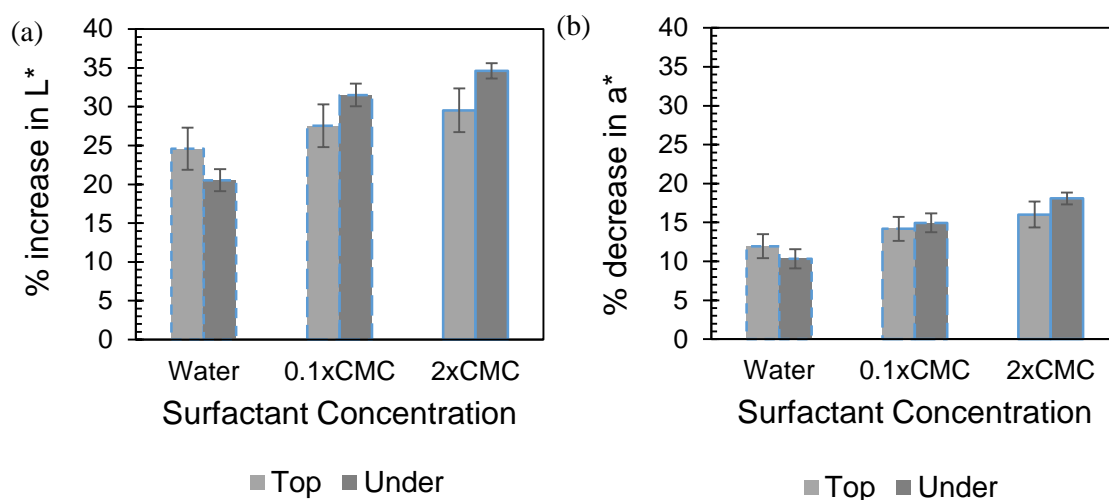


Figure 7.15. Comparison of the colour of the top and underside of polyester soiled with sebum cleaned using the rubbing rig at 20 °C with water and surfactant at a concentration of 0.1 x and 2 x CMC. Colour is measured as (a) L* and (b) a*. The error bars represent \pm one standard deviation for three fabrics. Five measurements were taken from each fabric.

Mass per unit area

Mass per unit area results of the fabrics rubbed with the three surfactant concentrations are presented in Figure 7.16. It can be seen that removal from the central strip is highest for fabrics rubbed with surfactant, and a lower mass loss is seen for the fabric rubbed in water. The fabrics are seen to have a lower mass than the original fabric on the unsoiled area, which is likely to be due to stretching of the fabric while it is rubbed. Removal is significantly greater than soaking alone, shown in Figure 5.14. On the strip adjacent to the soiled area the fabrics rubbed in water and 0.1 times the CMC of the surfactant solution increase in mass. This may be due to spreading of sebum from the central strip. It is likely that spreading also occurs for twice the CMC, but the sebum is subsequently removed.

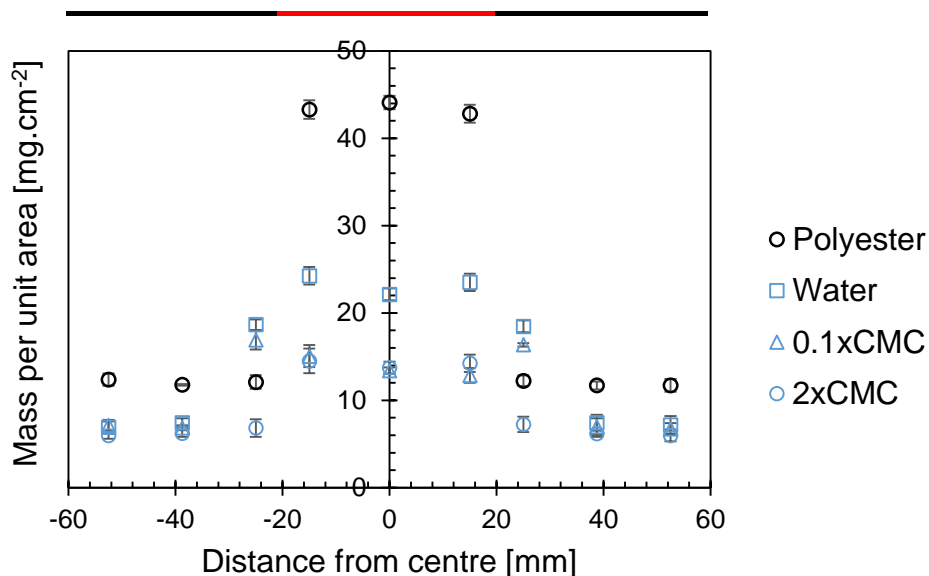


Figure 7.16. Mass per unit area of polyester soiled with sebum cleaned using the rubbing rig at 20 °C with water and surfactant at a concentration of 0.1 x and 2 x CMC. The error bars represent \pm one standard deviation for three fabrics.

FTIR

Figure 7.17 shows FTIR results for polyester rubbed in 20 °C wash solutions. It can be seen that on both the topside and underside there are only small differences between the three samples. All three fabrics show a reduction in the size of the sebum peaks and some polyester peaks that were previously masked can now be seen. Interestingly, the polyester peaks at 1240 and 1090 cm^{-1} are more pronounced when water is used, and are somewhat masked again when surfactant is used suggesting the surfactant monomer absorbs onto the surface and causes this masking.

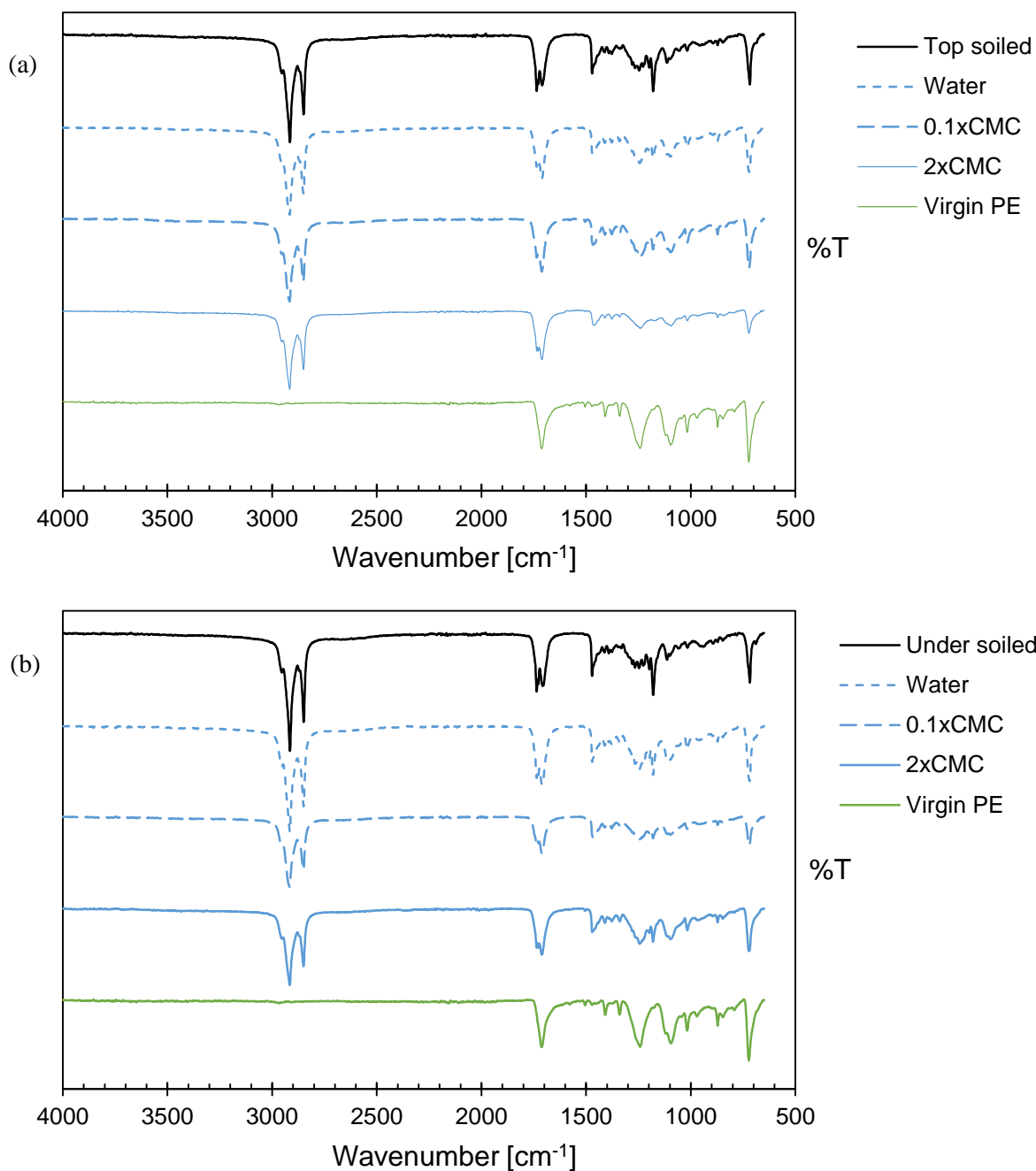


Figure 7.17. FTIR of polyester soiled with sebum cleaned using the rubbing rig at 20 °C with water and surfactant at a concentration of 0.1 x and 2 x CMC. This is compared to soiled and virgin polyester for both the (a) top and (b) underside of the fabric.

SEM

Fabrics imaged by SEM, Figure 7.18, show very little difference between samples rubbed with 2 x CMC and 0.1 x CMC at 20 °C, with both images showing some greasy sebum bridging gaps

between fibres at x500 magnification. This is consistent with the small difference in removal results found under these conditions.

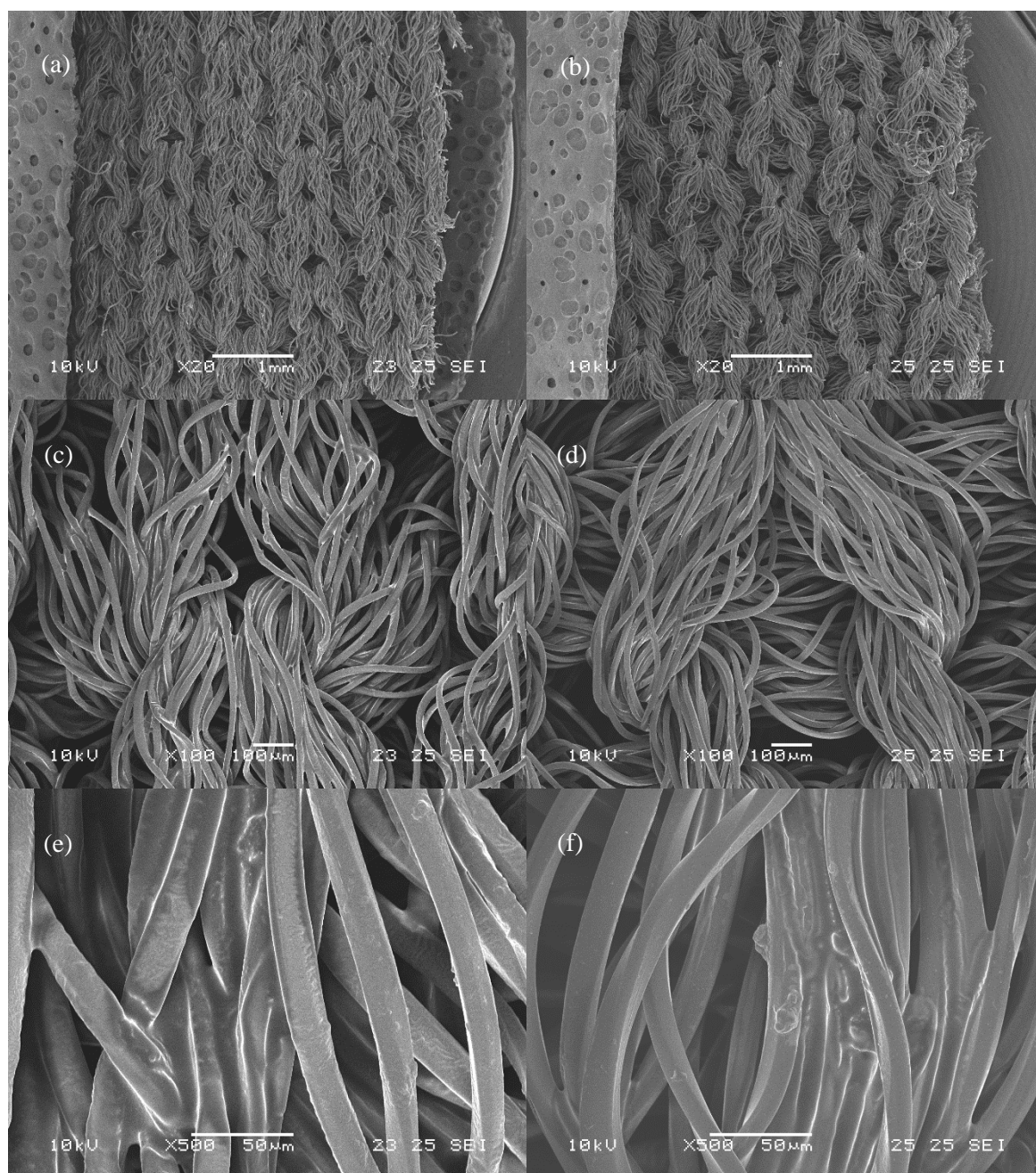


Figure 7.18. SEM images of soiled polyester rubbed in 20 °C surfactant solution at (a, c, e) 0.1 x CMC and (b, d, f) 2 x CMC at (a, b) x20 (c, d) x100 and (e, f) x500 magnifications.

However there are quite striking differences between samples than have been rubbed compared to those that have just been soaked. Figure 7.19 below shows samples washed in 20 °C wash solution with 2 x CMC. At all magnifications large quantities of sebum can be seen occupying pores, in

particular the intra yarn pores, on the sample that has been soaked. In comparison there is very little sebum on the sample that has been rubbed.

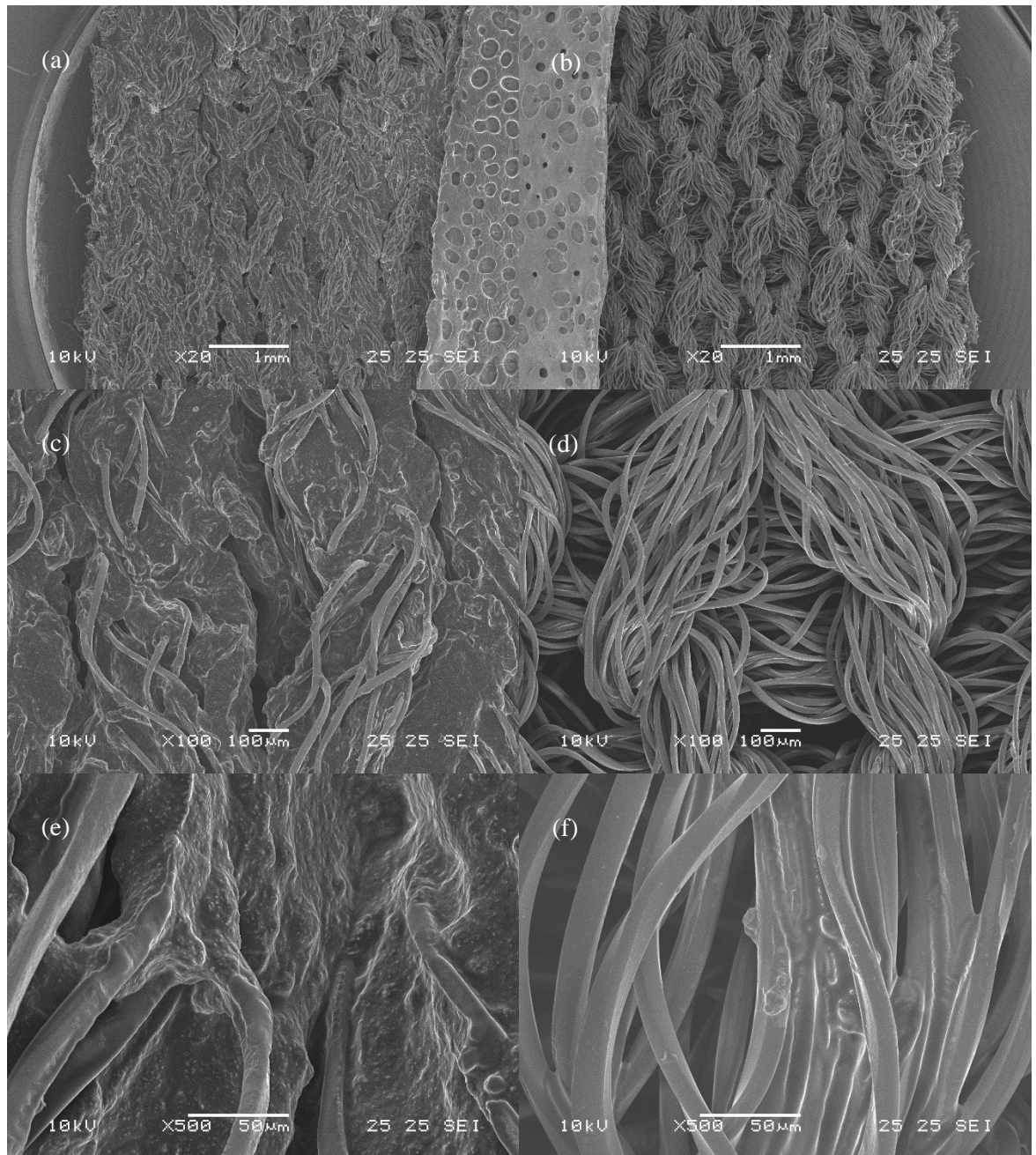


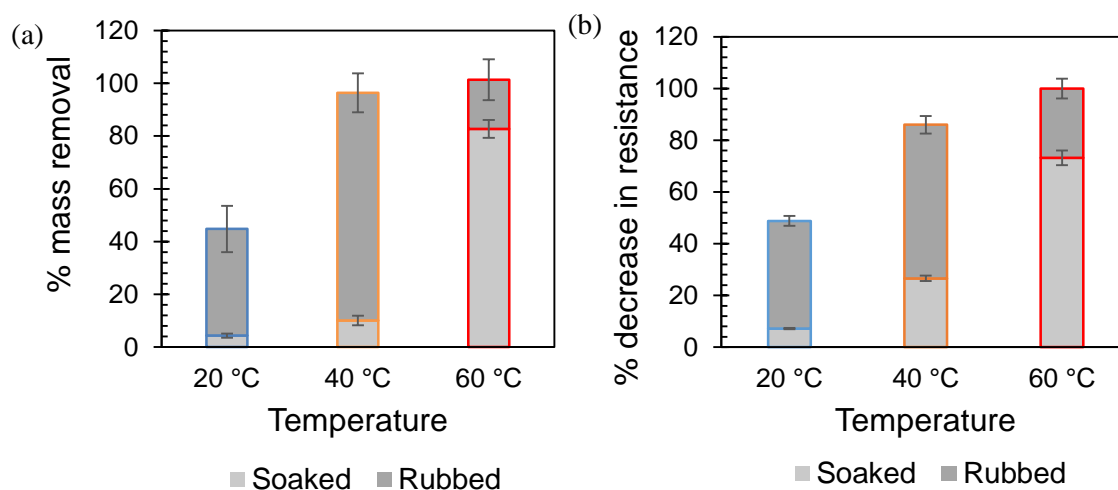
Figure 7.19. SEM images of soiled polyester (a, c, e) soaked and (b, d, f) rubbed with 20 °C 2 x CMC surfactant solution at (a, b) x20 (c, d) x100 and (e, f) x500 magnifications.

7.1.2 Cotton

7.1.2.1. Effect of Temperature

Mass, colour and resistance measurements

When rubbing is used in combination with surfactant at twice the CMC on cotton over a range of temperatures it can be seen that removal increases with increasing temperature, as shown in Figure 7.20. Removal from soaking at 60 °C is very high, so the additional action of rubbing only adds a small amount to the overall cleaning. However, at 40 °C a much greater benefit is seen when rubbing is used, and cleaning is then only slightly worse than at 60 °C. The increase in removal at 20 °C is smaller, but still significant. This suggests there is a synergistic effect when rubbing is used at 40 °C.



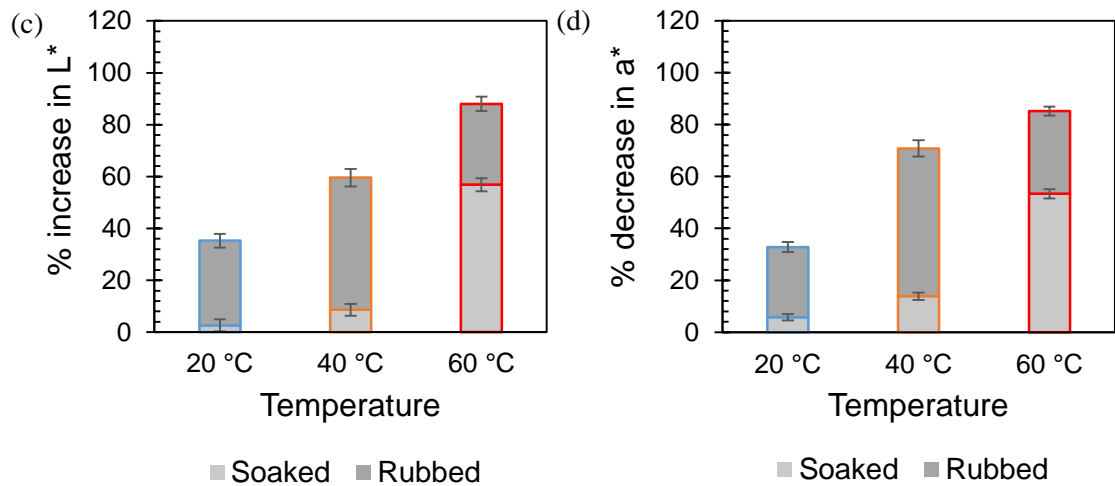


Figure 7.20. Effect of temperature on rubbing of cotton soiled with sebum. Surfactant was used at a concentration of 2 x CMC. Cleaning is measured by (a) % mass removal, (b) % decrease in resistance, (c) % increase in L^* and (d) % decrease in a^* . The error bars represent \pm one standard deviation for three fabrics. Five measurements were taken from each fabric for colour and resistance.

Colour of top and underside of fabric

Figure 7.21 shows the difference in removal from the topside and underside of the fabric. It can be seen that removal from the underside follows the same trend as removal from the top surface, with removal increasing with increasing temperature. In contrast to results found with polyester in Section 7.1.1.1, removal is consistently lower on the underside of the fabric. This is likely to be because the rubbing action is on the topside of the fabric therefore removal is primarily from this side.

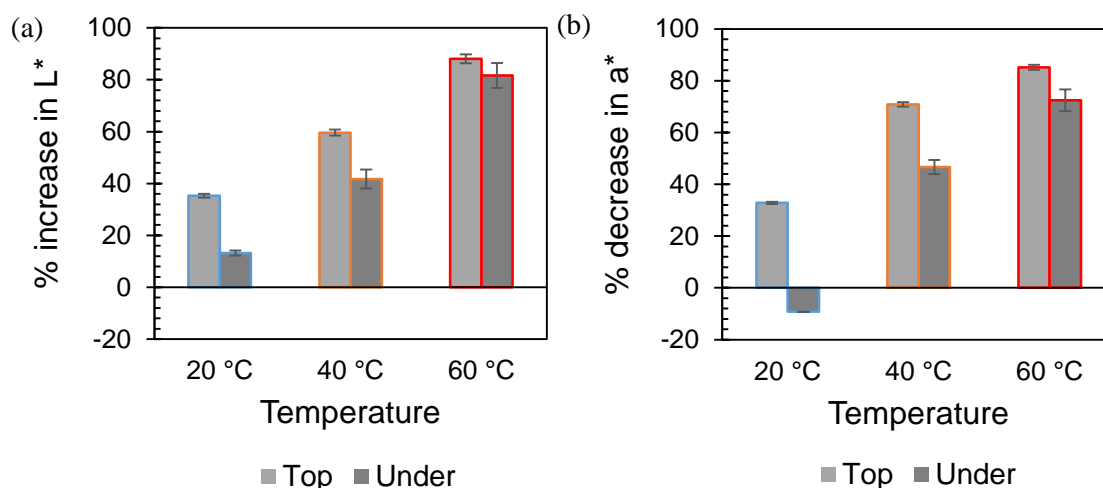


Figure 7.21. Comparison of the colour of the top and underside of cotton soiled with sebum cleaned using the rubbing rig at 20 °C, 40 °C and 60 °C with surfactant at a concentration of 2 x CMC. Colour is measured as (a) L^* and (b) a^* . The error bars represent \pm one standard deviation for three fabrics. Five measurements were taken from each fabric.

Mass per unit area

Mass per unit area results are in line with previous mass loss results, as shown in Figure 7.22. At 60 °C removal gives a mass per unit area very similar to the virgin fabric. Removal at 40 °C is slightly less, and removal is lowest at 20 °C. No significant spreading of sebum can be seen on the surrounding area of virgin fabric. Unlike polyester, the mass of the clean area of fabric does not significantly decrease, although a slight decrease is seen. This is likely to be because the cotton is not as stretchy as the polyester in the first place, so mass per unit area is not dramatically reduced when the fabric is stretched in the rig prior to rubbing.

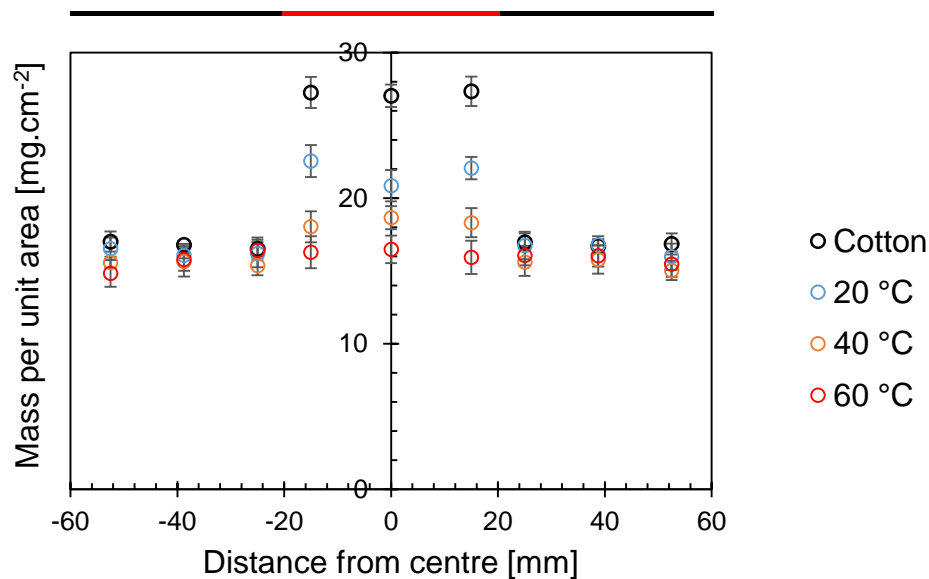


Figure 7.22. Mass per unit area of cotton soiled with sebum cleaned using the rubbing rig at 20 °C, 40 °C and 60 °C with surfactant at a concentration of 2 x CMC. The error bars represent \pm one standard deviation for three fabrics.

FTIR

Figure 7.23 shows the FTIR of the topside and underside of fabrics rubbed at the various temperatures. Cotton peaks can be seen at all temperatures with very little masking of peaks observed, but sebum peaks, for example those at 2900 and 2830 cm^{-1} , are significantly reduced on all samples. Some sebum peaks, such as at 1730 cm^{-1} , are not visible at all when the fabric is rubbed at temperatures above 40 °C.

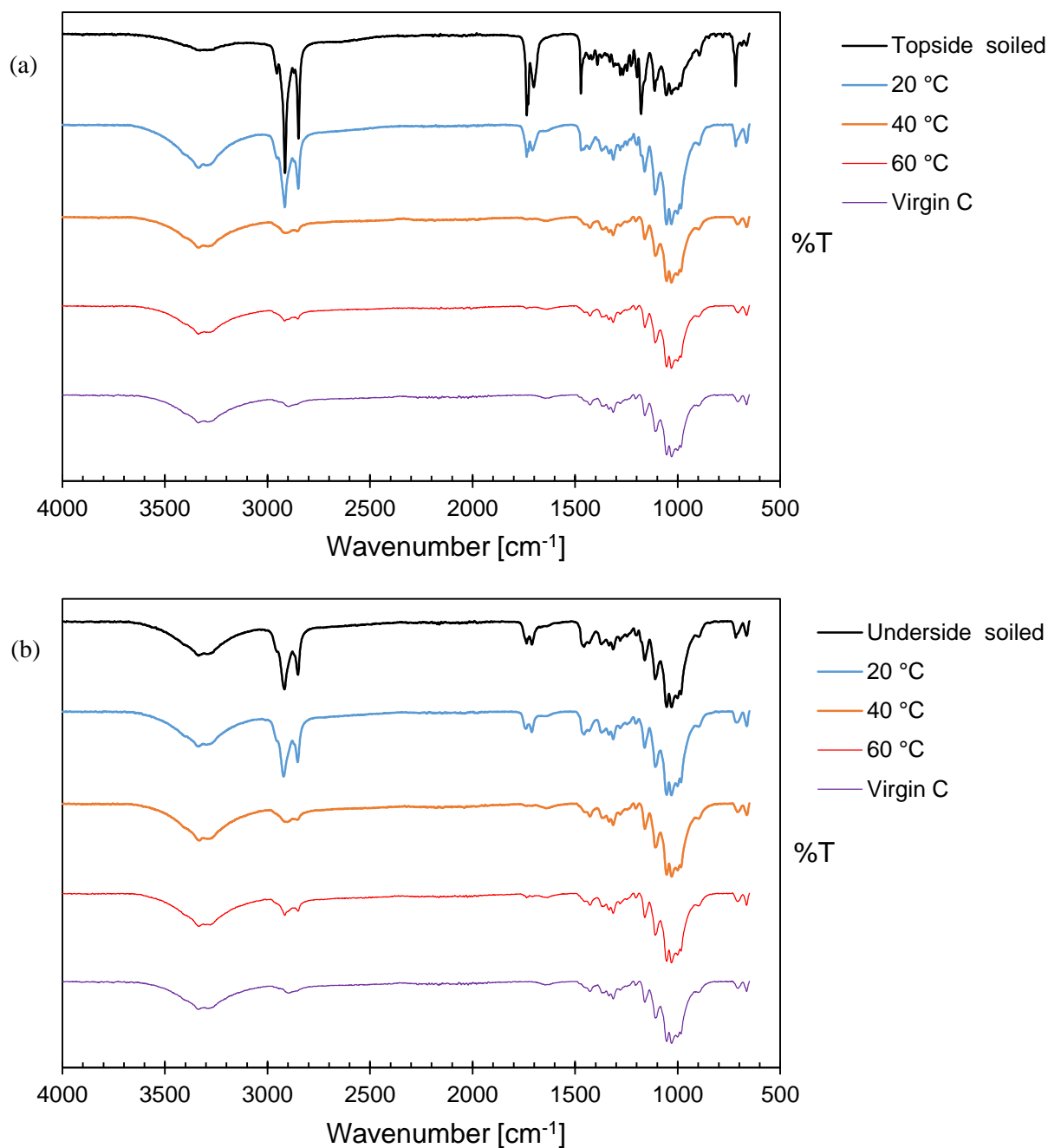


Figure 7.23. FTIR of cotton soiled with sebum cleaned using the rubbing rig at 20 °C, 40 °C and 60 °C with surfactant at a concentration of 2 x CMC. This is compared to soiled and virgin cotton for both the (a) top and (b) underside of the fabric.

Zeta Potential

Zeta potential results, shown in Figure 7.24, are much more as expected than polyester zeta potential results. It would be expected that the most cleaned samples are similar to virgin fabric, and the

samples with the most soil are most similar to soiled polyester. All samples lie within the soiled and virgin cotton, with the lowest removal at 20 °C more similar to soiled cotton, and the other two temperatures very similar to each other and to virgin cotton. This is in line with mass removal results.

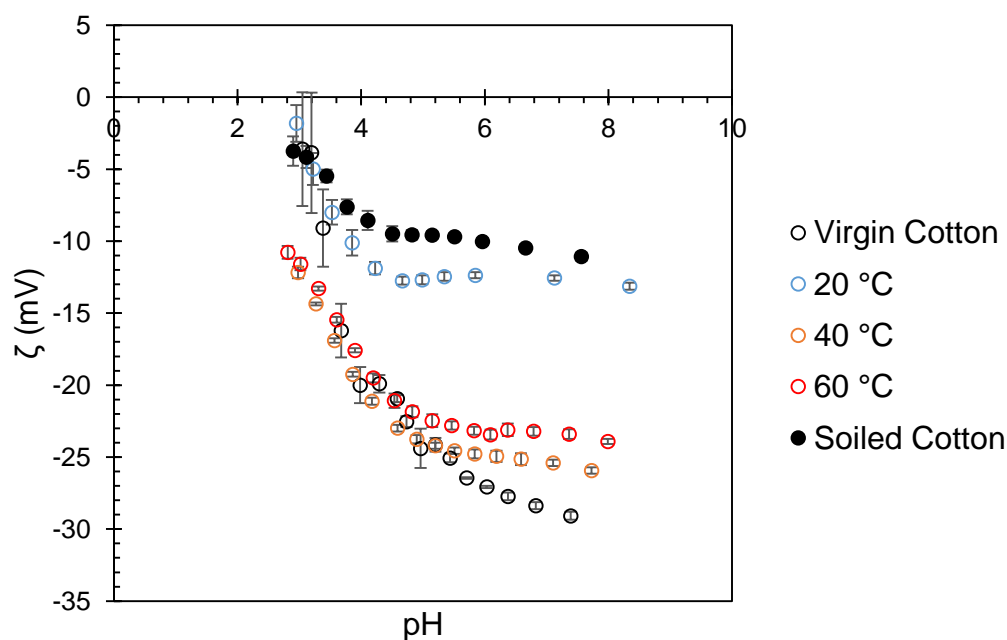
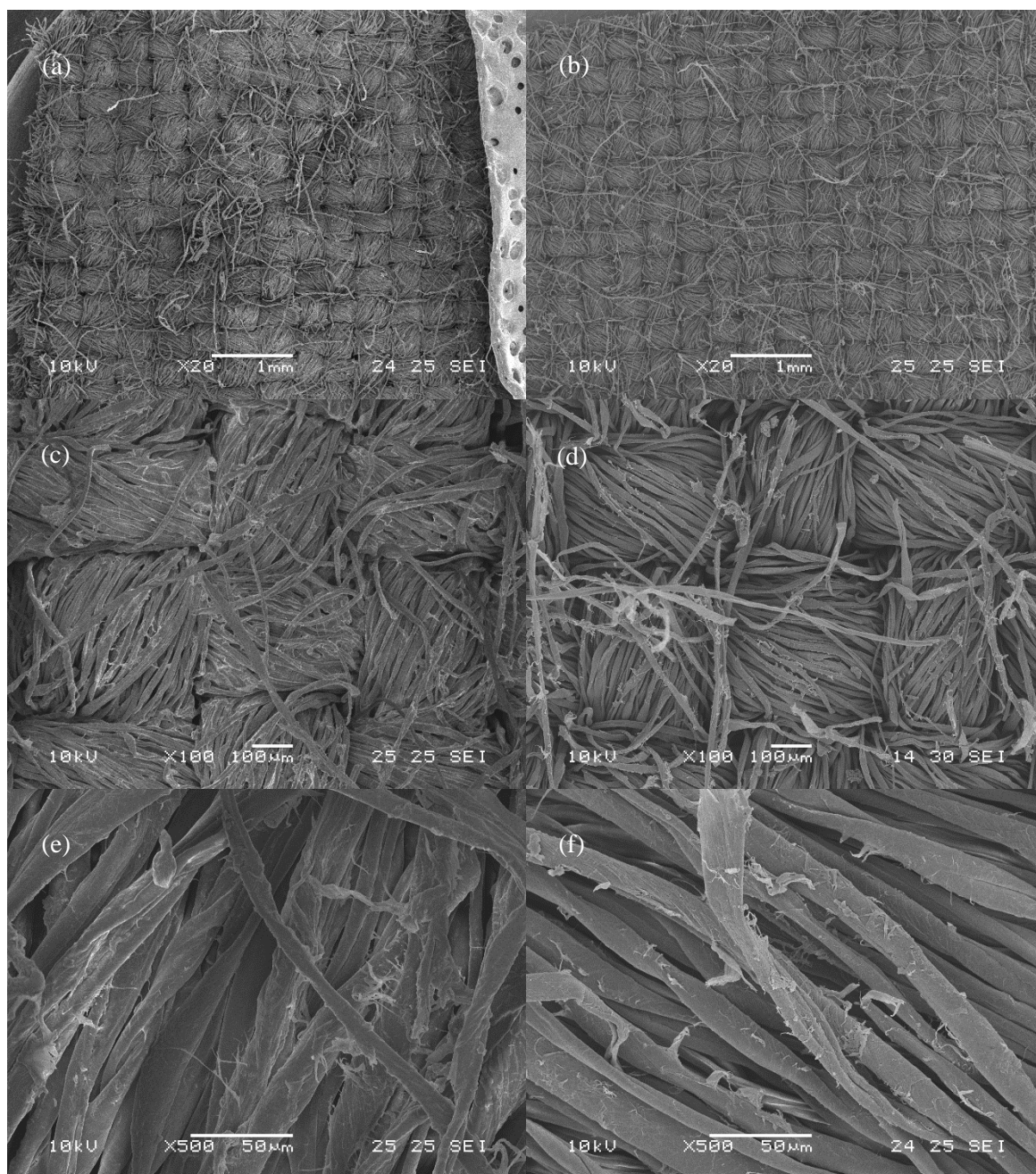


Figure 7.24. Effect of temperature on zeta potential for cotton soiled with sebum and rubbed at 20 °C, 40 °C and 60 °C with surfactant at a concentration of 2 x CMC. The error bars represent \pm one standard deviation for four repeat measurements taken on each fabric.

SEM

SEM images were taken for cotton rubbed at 20 °C and 60 °C with 2 x CMC, as shown in Figure 7.25. The two fabrics look similar at x20 magnification, however at x100 the sample washed at 60 °C appears significantly cleaner. On the x500 and x1000 images much more of the granular soil can be seen on and between fibres from the sample cleaned at 20 °C. This fits with results found previously.



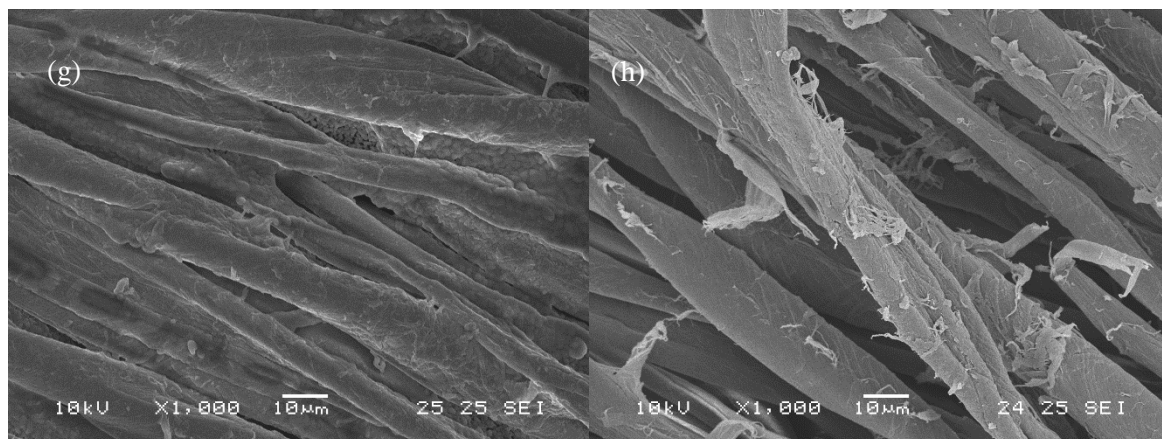


Figure 7.25. SEM images of soiled cotton rubbed with 2 x CMC surfactant solution at (a, c, e, g) 20 °C and (b, d, f, h) 60 °C at (a, b) x20, (c, d) x100, (e, f) x500 and (g, h) x1000 magnifications.

7.1.2.2. Effect of surfactant concentration at 40 °C

Mass, colour and resistance measurements

Figure 7.26 shows removal of sebum rubbed at 40 °C in different wash solutions. It can be seen that removal is higher when twice the CMC of the surfactant is used, and a small benefit is seen when 0.1 times the CMC is used. The decrease in resistance seen with rubbing is approximately equal for all three conditions, which suggests that the rubbing action is removing sebum from the pores regardless of surfactant concentration, whereas removal on the surface may be much more dependent on surfactant concentration.

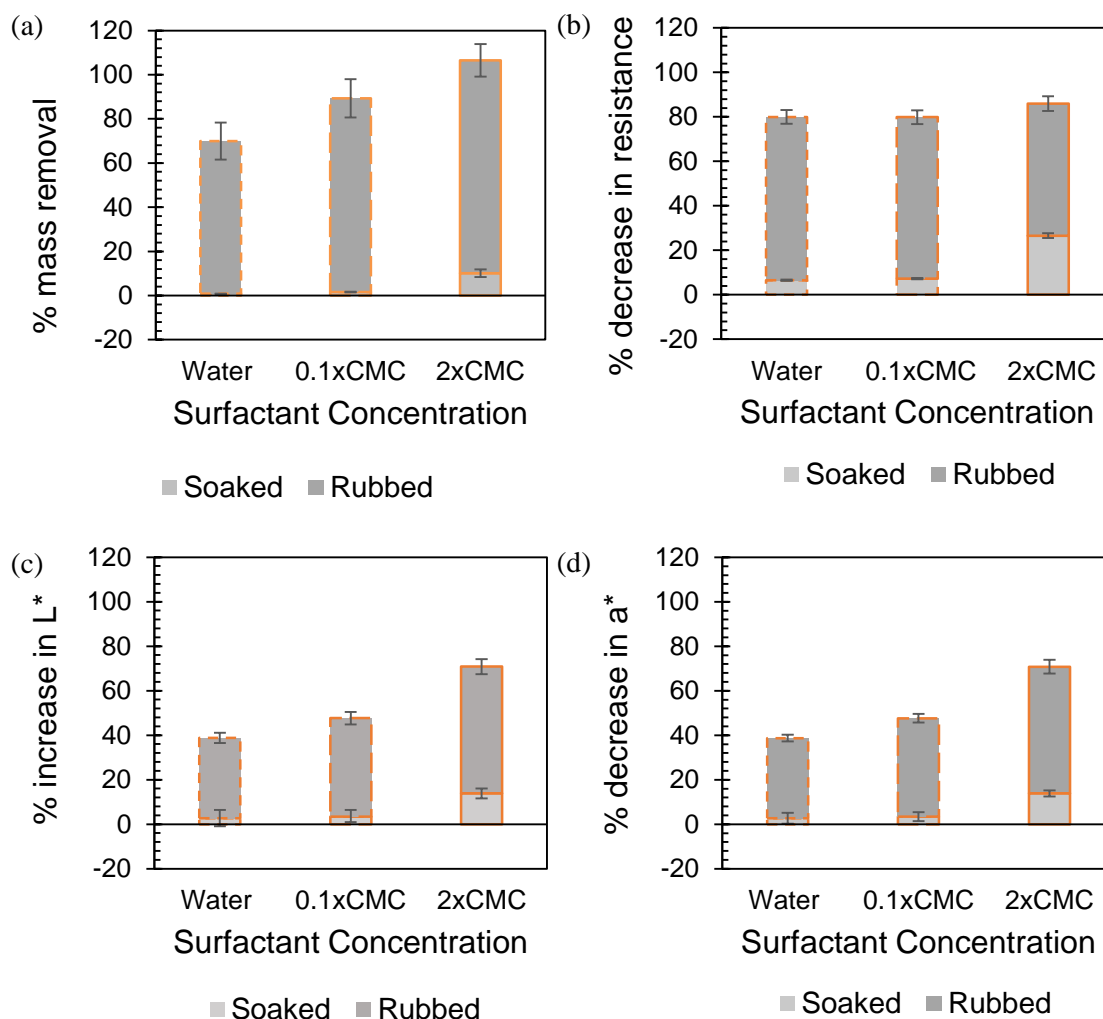


Figure 7.26. Effect of surfactant concentration on rubbing at 40 °C for cotton soiled with sebum. Cleaning is measured by (a) % mass removal, (b) % decrease in resistance, (c) % increase in L^* and (d) % decrease in a^* . The error bars represent \pm one standard deviation for three fabrics. Five measurements were taken from each fabric for colour and resistance.

Colour of top and underside of fabric

When the colour of topside and underside of the fabric are compared, as in Figure 7.27, it can be seen that removal from the underside is in line with removal from the top side, although the amount of removal is much less. Again, this is likely to be because the action of rubbing is against the top side of the fabric, and in fact the rubbing blade may force some sebum on the underside of the fabric further embedded into the fabric preventing removal.

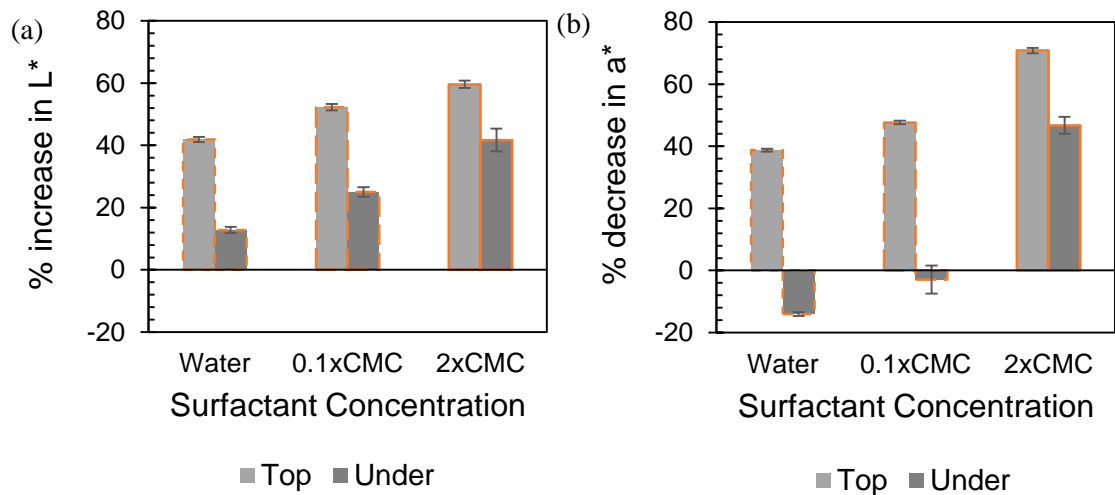


Figure 7.27. Comparison of the colour of the top and underside of cotton soiled with sebum cleaned using the rubbing rig 40 °C with surfactant at a concentrations of 0.1 x CMC and 2 x CMC as well as water. Colour is measured as (a) L* and (b) a*. The error bars represent \pm one standard deviation for three fabrics. Five measurements were taken from each fabric.

Mass per unit area

Figure 7.28 shows the mass per unit area of the fabrics after rubbing. Again, removal results are in line with mass removal observed previously, with water showing the least removal. No spreading of the sebum is observed in the clean area of the fabric adjacent to the soiled strip. A small decrease in mass of the clean area of the rubbed fabric is observed, which is due to stretching of the fabric in the rig. Again, this decrease in mass is much smaller than that observed for polyester.

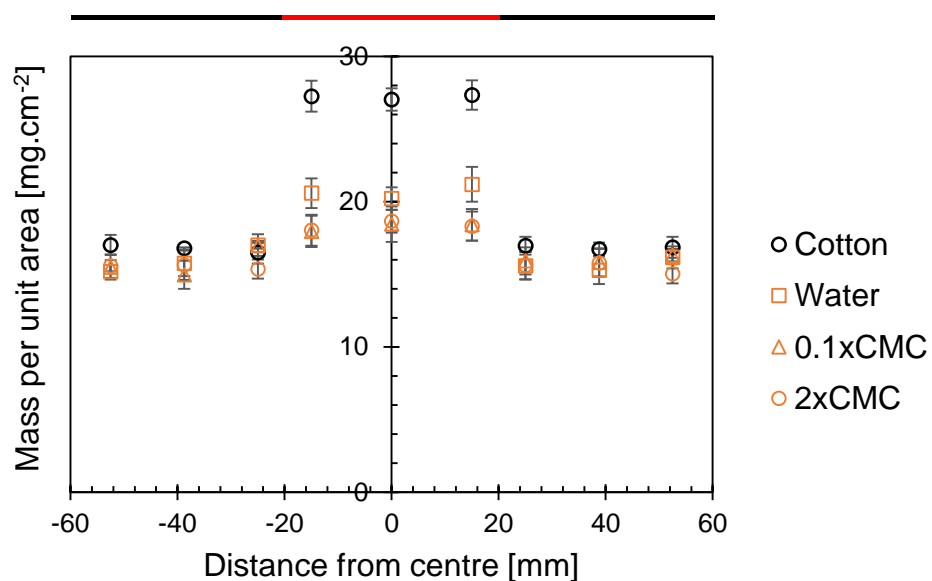
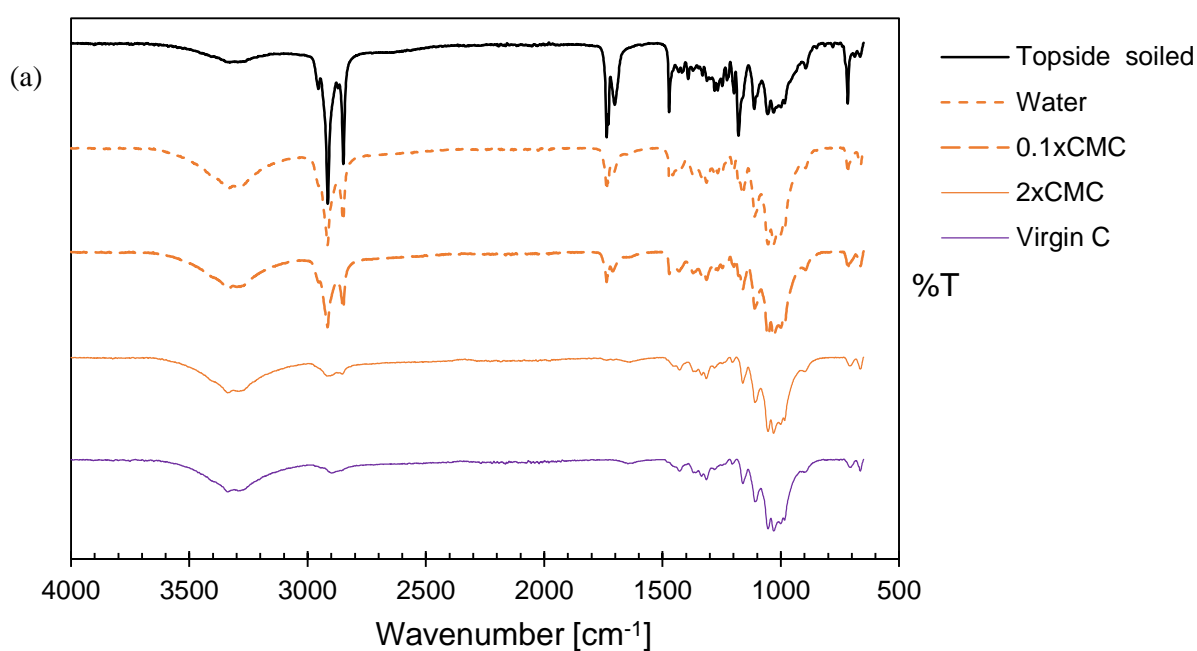


Figure 7.28. Mass per unit area of cotton soiled with sebum cleaned using the rubbing rig at 40 °C with water and surfactant at a concentration of 0.1 x and 2 x CMC. The error bars represent \pm one standard deviation for three fabrics.

FTIR

FTIR spectra, presented in Figure 7.29, show reduction in the size of the sebum peaks as concentration of surfactant is increased on both the topside and underside of the cotton. The cotton peak at 3300 cm^{-1} that is somewhat masked on the topside soiled spectrum is much more pronounced on all three of the rubbed samples, indicating a significant amount of sebum has been removed from the top surface of the cotton.



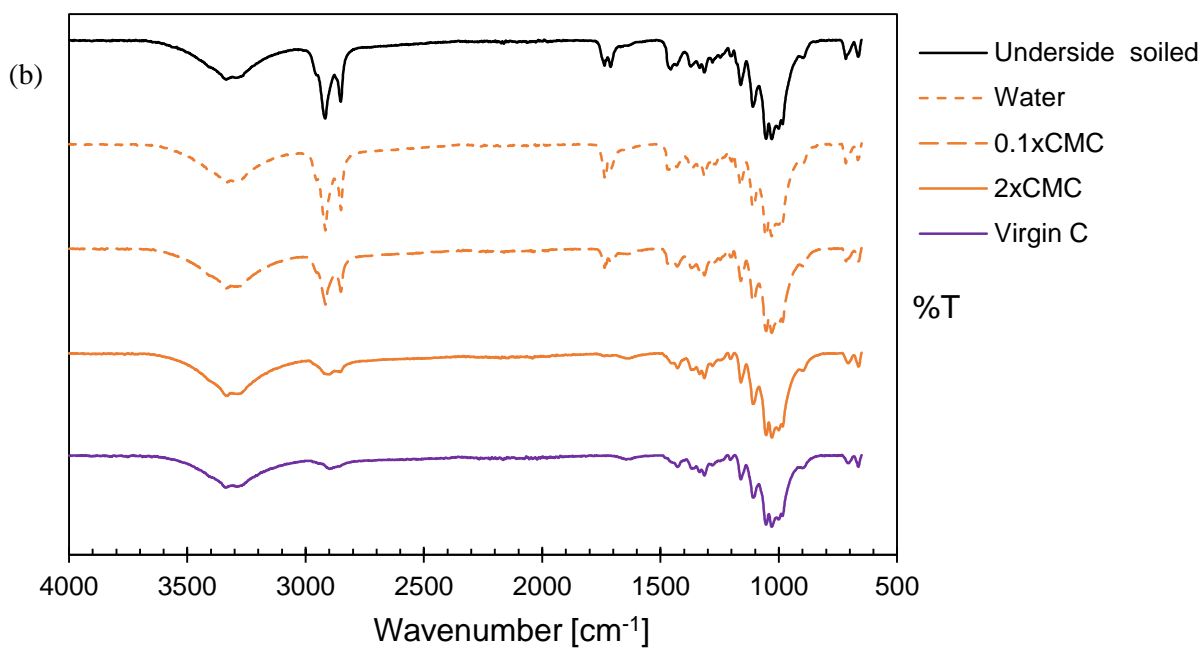


Figure 7.29. FTIR of cotton soiled with sebum cleaned using the rubbing rig at 40 °C with water and surfactant at a concentration of 0.1 x and 2 x CMC. This is compared to soiled and virgin cotton for both the (a) top and (b) underside of the fabric.

Zeta Potential

Zeta potential results, presented in Figure 7.30, show that the surface charge of the three rubbed fabrics is between the surface charges of virgin and soiled cotton. The most cleaned sample, when twice the CMC of the surfactant is used, is most similar to virgin cotton, and the least cleaned sample rubbed with only water is most similar to virgin cotton. This is as expected and is in line with removal results presented previously.

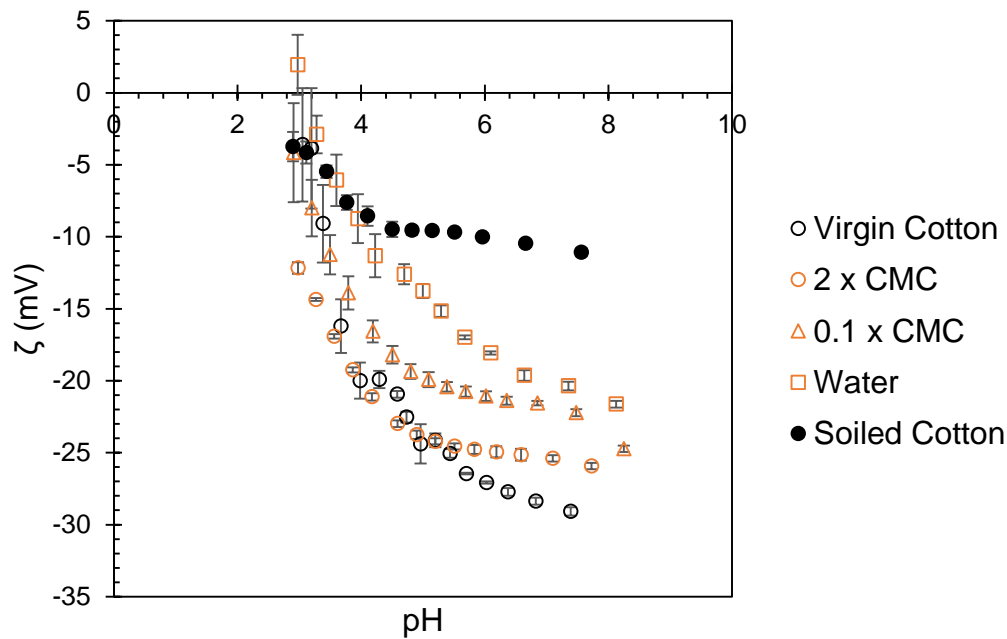


Figure 7.30. Effect of surfactant concentration on zeta potential for cotton soiled with sebum and rubbed at 40 °C with surfactant solution at 0.1 x CMC and 2 x CMC as well as water. The error bars represent \pm one standard deviation for four repeat measurements taken on each fabric.

Virgin cotton was also tested to investigate the effect of rubbing on the surface charge of the fabric.

Figure 7.31 shows rubbing the virgin cotton surface decreases the magnitude of the negative zeta potential. It is suspected that the rubbing action has removed some sort of coating or detergent molecules left on the fabric after desizing.

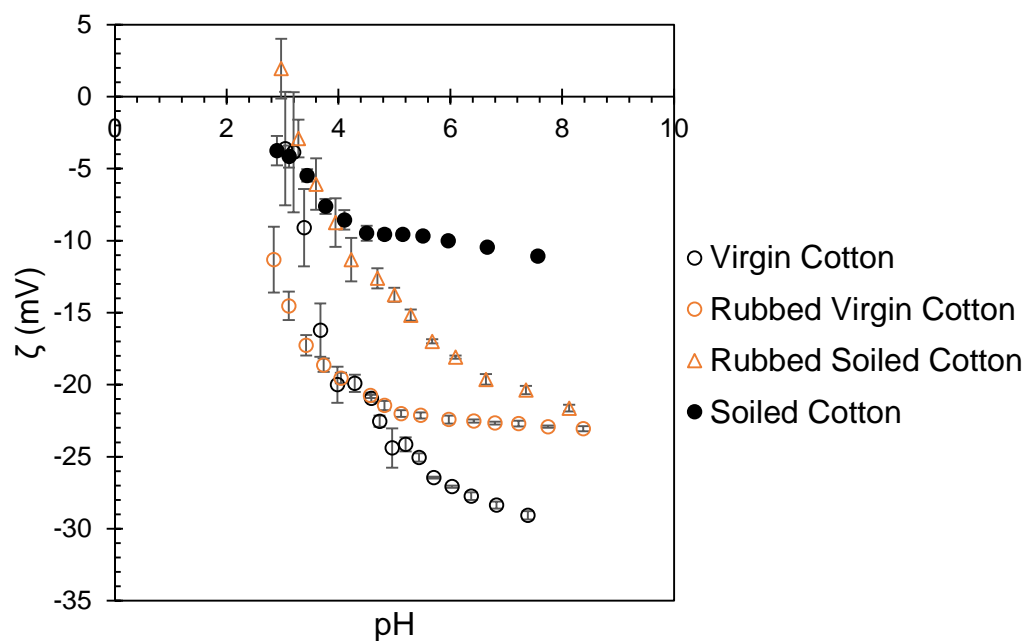


Figure 7.31. Comparing the zeta potential of virgin and soiled cotton fabrics rubbed in 40 °C water. The error bars represent \pm one standard deviation for four repeat measurements taken on each fabric.

FTIR was also used to investigate the surface of rubbed virgin cotton, to see if the change in zeta potential could be observed as a change in the chemical makeup of the surface. It can be seen that there are no real differences between the virgin cotton and rubbed virgin cotton. It is thought that FTIR may not be sufficiently sensitive to show differences between these samples.

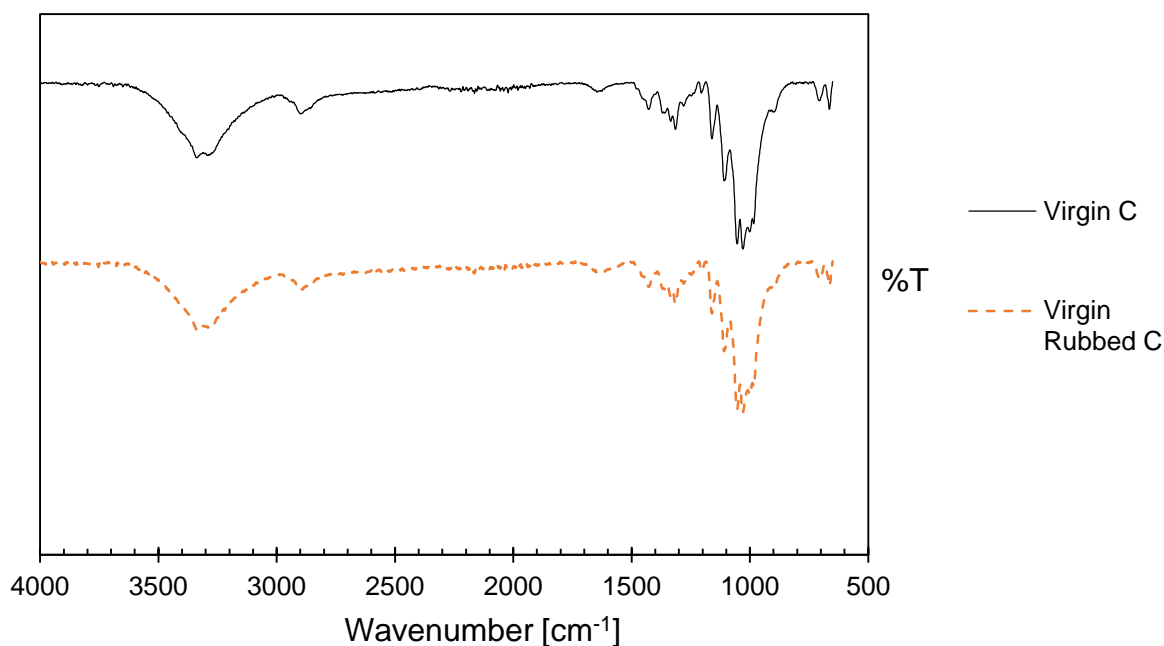


Figure 7.32. FTIR of virgin cotton rubbed in at water at 40 °C compared to virgin cotton.

7.1.2.3. Effect of surfactant concentration at 20 °C

Mass, colour and resistance measurements

As 20 °C an obvious difference can be seen when fabrics are rubbed with twice the CMC of the surfactant compared to 0.1 times the CMC or water, as shown in Figure 7.33. This suggests there is a synergistic effect between the surfactant at higher concentration and the rubbing action which aids removal. Rubbing may expose more sebum, which the surfactant can then remove via various mechanisms. There is no real difference between water and 0.1 times the CMC of the surfactant, so at this temperature there is no benefit to using a low concentration of surfactant.

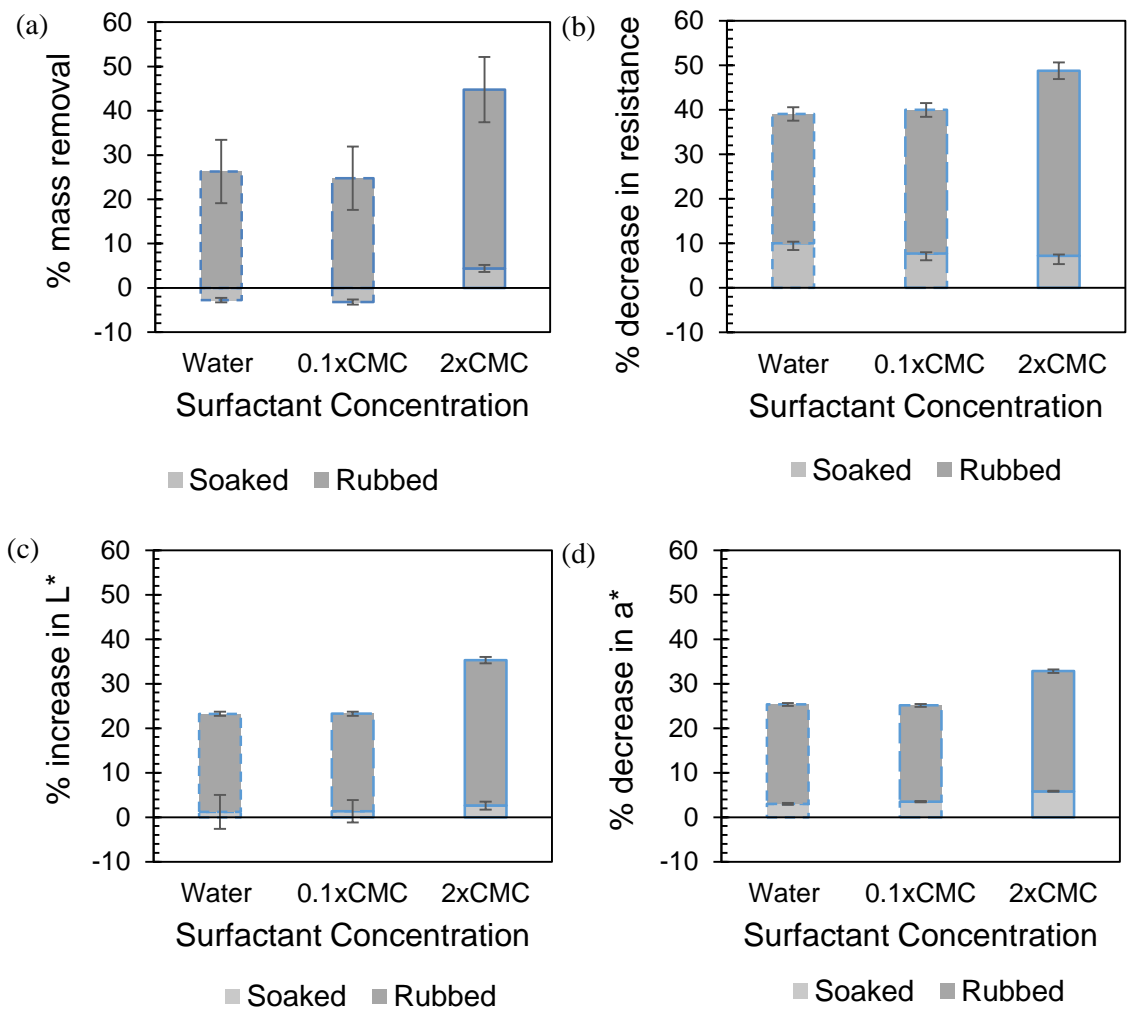


Figure 7.33. Effect of surfactant concentration on rubbing at 20 °C for cotton soiled with sebum. Cleaning is measured by (a) % mass removal, (b) % decrease in resistance, (c) % increase in L^* and (d) % decrease in a^* . The error bars represent \pm one standard deviation for three fabrics. Five measurements were taken from each fabric for colour and resistance.

Colour of top and underside of fabric

Figure 7.34 shows the colour of the topside and underside of the fabric rubbed at 20 °C. It can be seen that although the trend is the same as the topside, removal from the underside is much lower, and for some conditions the underside of the fabric at the end of the experiment is redder than the original soiled fabric. This suggests that the rubbing action may be pushing some of the soil from the topside through the fabric to increase the amount of sebum on the underside. This mechanism may occur at other temperatures, but removal overall is higher so this effect is somewhat masked.

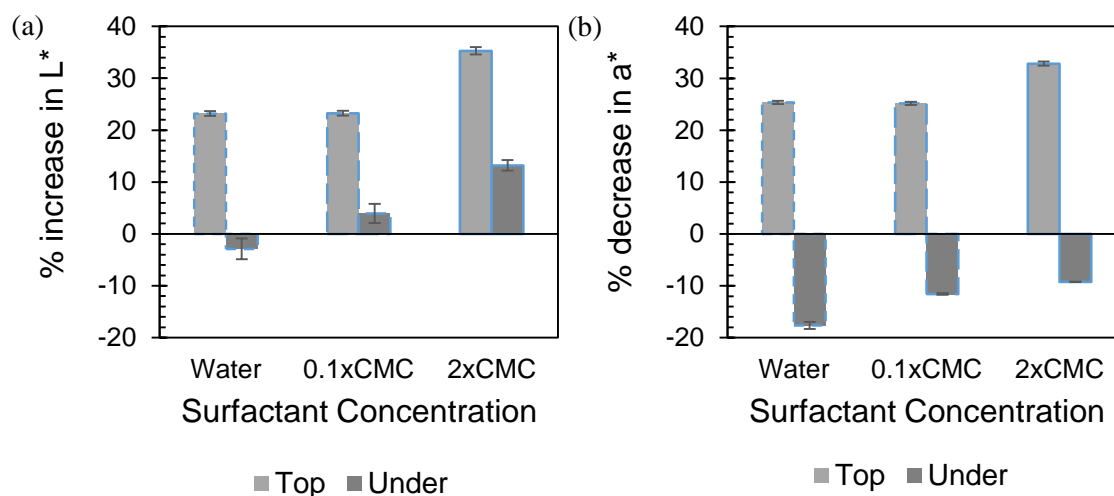


Figure 7.34. Comparison of the colour of the top and underside of cotton soiled with sebum cleaned using the rubbing rig at 40 °C with water and surfactant at a concentration of 0.1 x and 2 x CMC. Colour is measured as (a) L* and (b) a*. The error bars represent \pm one standard deviation for three fabrics. Five measurements were taken from each fabric.

Mass per unit area

Mass per unit area results, as shown in Figure 7.35, show that removal is highest when twice the CMC of surfactant is used, in line with results seen previously. Removal is very similar when 0.1 times the CMC or water alone are used. A slight decrease in mass per unit area is observed on the clean area of the fabric, which is due to stretching of the fabric during testing.

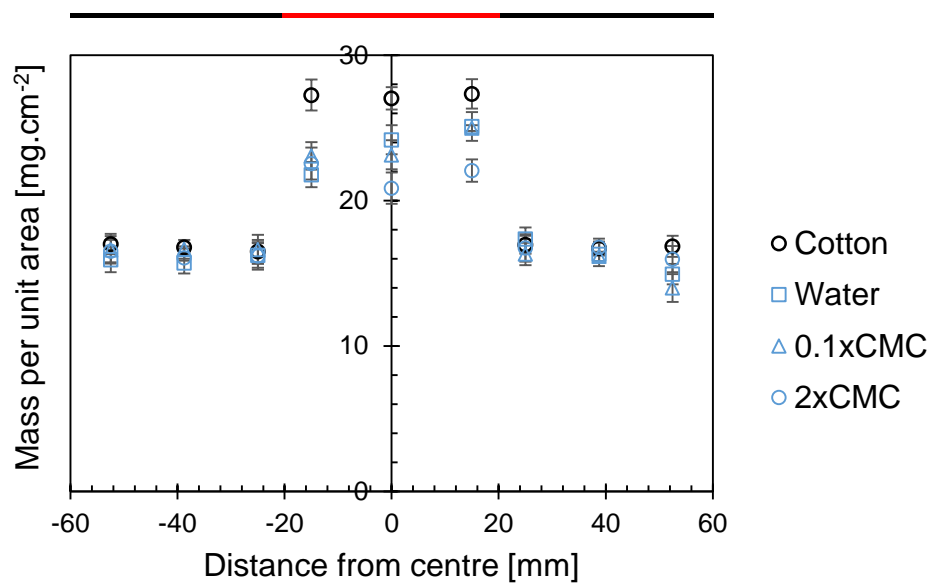


Figure 7.35. Mass per unit area of cotton soiled with sebum cleaned using the rubbing rig at 20 °C with water and surfactant at a concentration of 0.1 x and 2 x CMC. The error bars represent \pm one standard deviation for three fabrics.

FTIR

Figure 7.36 shows FTIR spectra for rubbed fabrics at 20 °C. The distinctive sebum peaks at 2900 and 2850 cm⁻¹ are much smaller when twice the CMC is used when compared to the other conditions tested. On the underside of the fabric it can be seen that these peaks have increased in size when compared to the soiled underside of cotton, which supports colour results presented above which suggest some sebum has been pushed through the fabric to the underside by the force of the rubbing blade.

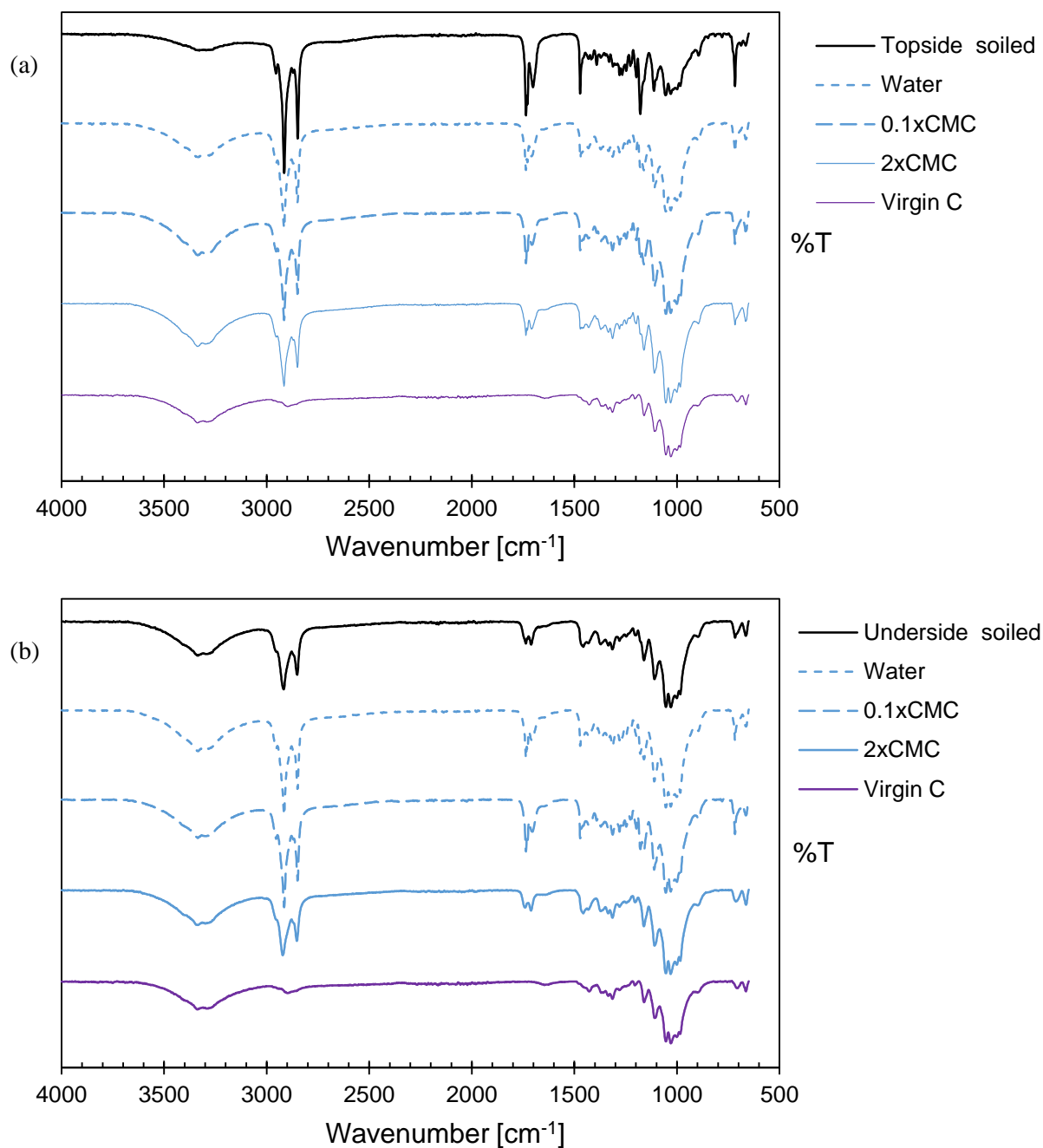


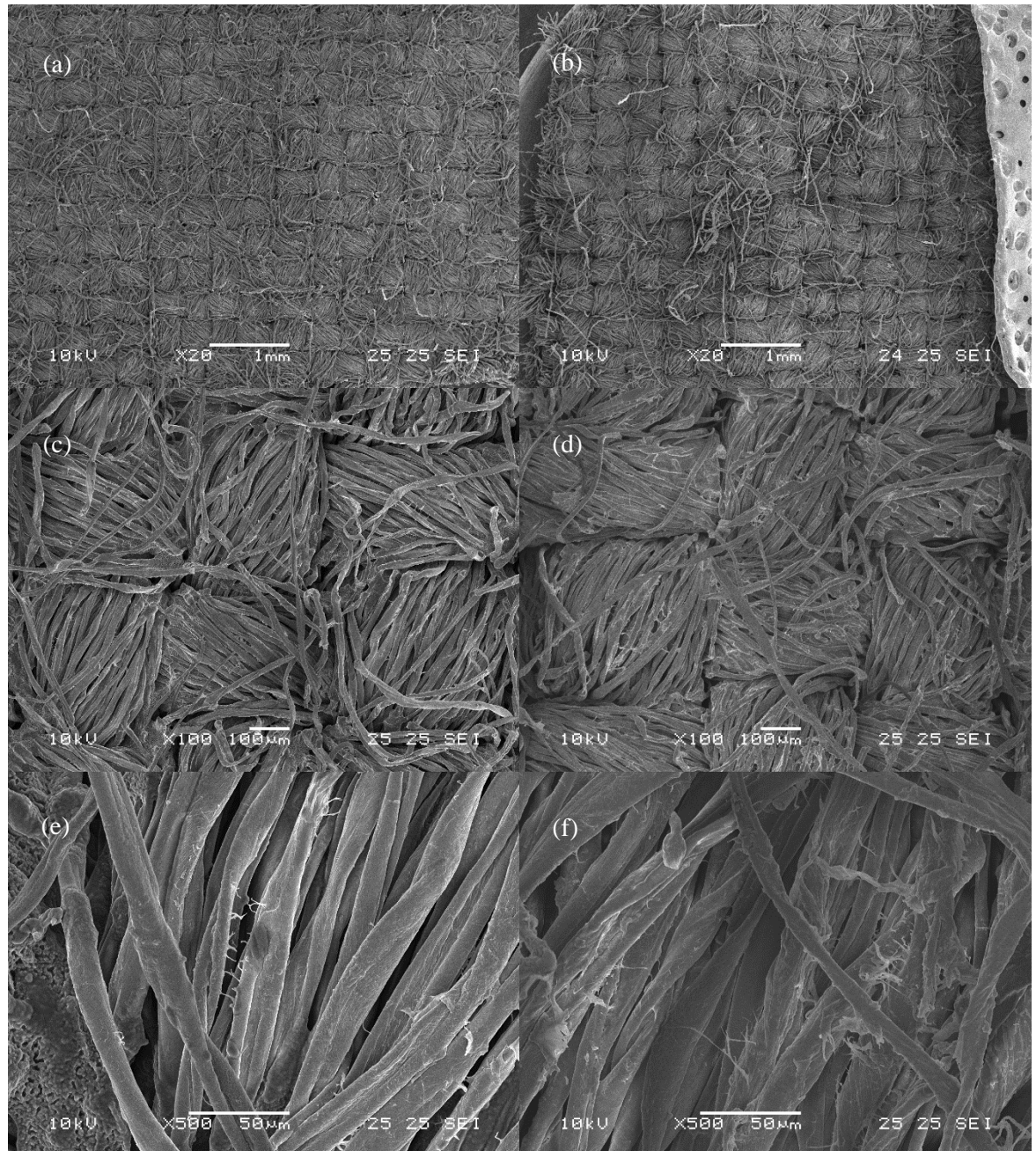
Figure 7.36. FTIR of cotton soiled with sebum cleaned using the rubbing rig at 20 °C with water and surfactant at a concentration of 0.1 x and 2 x CMC. This is compared to soiled and virgin cotton for both the (a) top and (b) underside of the fabric.

SEM

SEM images comparing 0.1 x CMC and 2 x CMC surfactant solutions are shown in Figure 7.37.

Images at x20 and x100 magnifications show very little differences. At x500, an area of sebum can be seen in the left of the image for 0.1 x CMC, with most of the fibres appearing fairly clean. A

similar distribution of sebum cannot be seen on the 2 x CMC image, however both fibres appear to be equally clean. A similar observation can be seen on the x1000 image, with more areas of sebum visible on the 0.1 x CMC image, however it is clear the sample at 2 x CMC is not completely clean either.



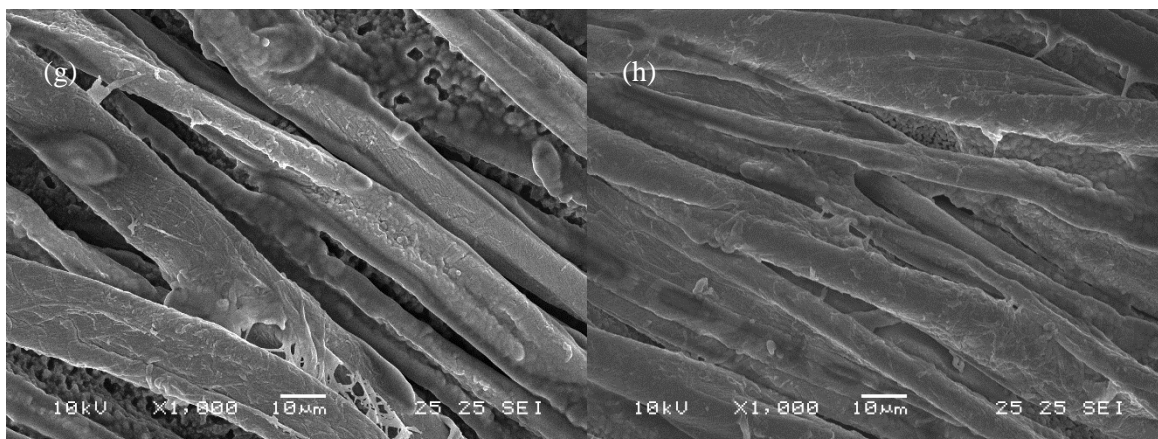
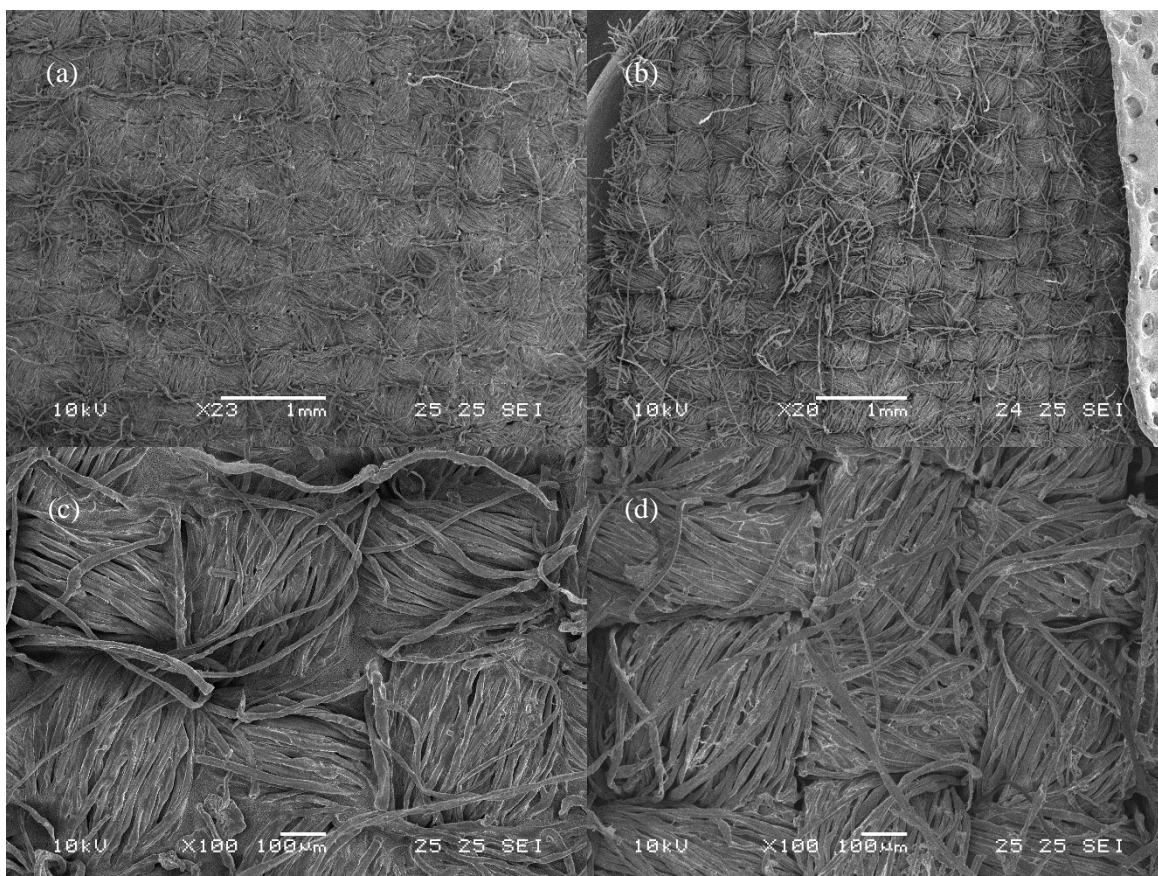


Figure 7.37. SEM images of soiled cotton rubbed in 20 °C surfactant solution at (a, c, e, g) 0.1 x CMC and (b, d, f, h) 2 x CMC at (a, b) x20, (c, d) x100, (e, f) x500 and (g, h) x1000 magnifications.

SEM images show a more significant difference between samples that have been soaked compared to those that have been rubbed, as shown in Figure 7.38. Sebum is clearly visible on the soaked images at x500 and x1000 magnifications, whereas the rubbed images show less sebum both coating the fibres and in between them.



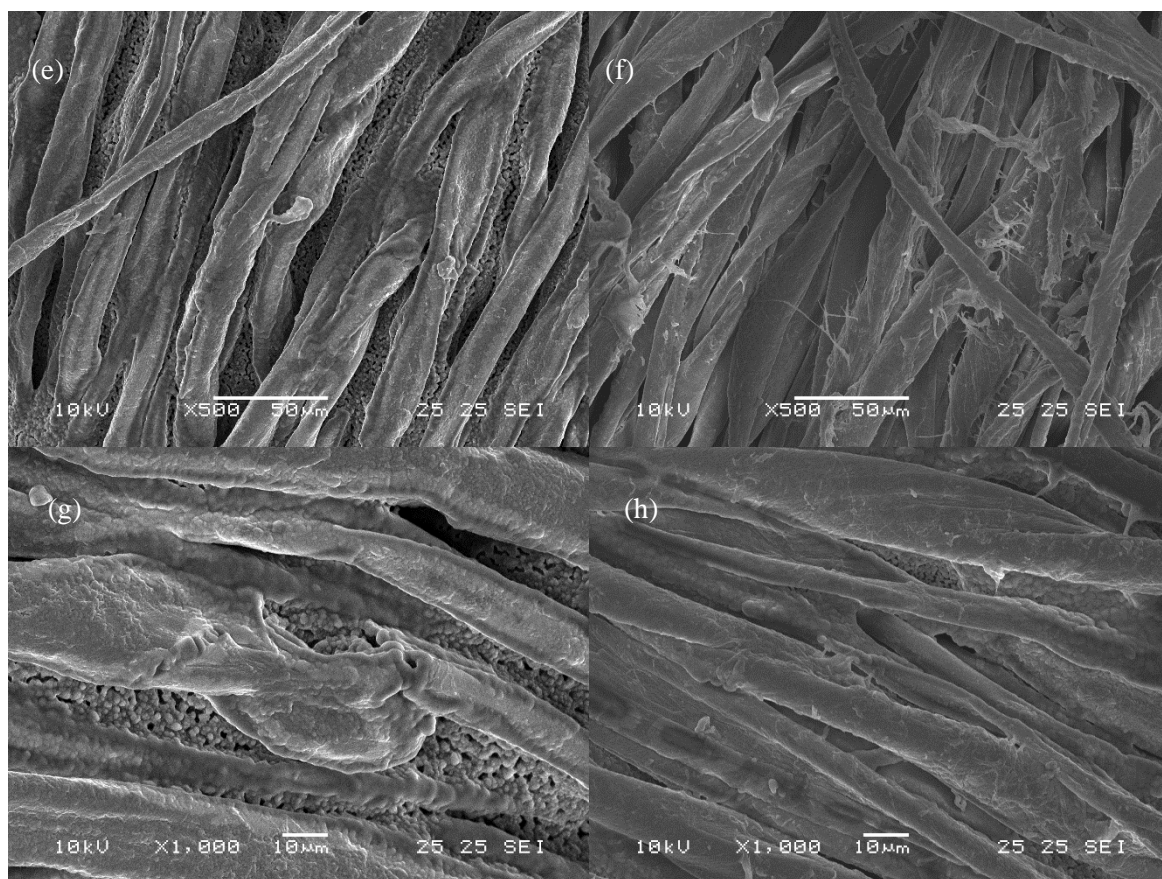


Figure 7.38. SEM images of soiled cotton (a, c, e, g) soaked and (b, d, f, h) rubbed with 20 °C 2 x CMC surfactant solution at (a, b) x20, (c, d) x100, (e, f) x500 and (g, h) x1000 magnifications.

7.1.3. Discussion on rubbing

For fabrics rubbed in twice the CMC of the surfactant removal of sebum increases with increasing temperature for both fabrics. For polyester, the increase in cleaning when compared to soaking alone is similar for all three temperatures. However, for cotton, the increase is much higher for fabrics washed at 40 °C, suggesting there is a synergistic effect when surfactant is used with rubbing. A smaller increase is seen at 60 °C, which may be because removal is already high at this temperature so there is less room for improvement. The difference in the two fabrics may be due to the fact that the sebum on the cotton sits mainly on the top side of the fabric, therefore it is accessible to the rubbing action. When used with 40 °C surfactant solution, the molten sebum allows for a greater benefit than is observed at 20 °C. Sebum on polyester has soaked through the fabric so both sides are almost equally soiled, and since the rubbing action is only on the top surface removal will mostly be

from this surface. The sebum on the underside is likely to be compressed into the fabric rather than removed.

When the effect of surfactant concentration is considered at 20 °C and 40 °C, removal from polyester increases with 0.1 times the CMC of the surfactant, and increases again when twice the CMC is used, suggesting there is a synergistic effect when rubbing is combined with surfactant. The same effect is observed with cotton at 40 °C. It is suspected that, even at low concentration, the surfactant is able to loosen the soil, aiding easier removal by the rubbing blade. This is likely to be by roll up as this mechanism is possible at low concentrations. Solubilisation is possible at higher concentrations therefore will additionally aid removal at higher concentrations. Interestingly, the same trend is not seen when cotton is rubbed in 20 °C surfactant solution. At this temperature a benefit is only observed when twice the CMC is used. This may be because the cotton is more hydrophobic due to its coating, therefore has greater affinity for the soil, and hence at the lower temperature a higher concentration of surfactant is required to loosen the soil. The surfactant is only working using mechanisms available at concentrations above the CMC.

7.2. Stretching

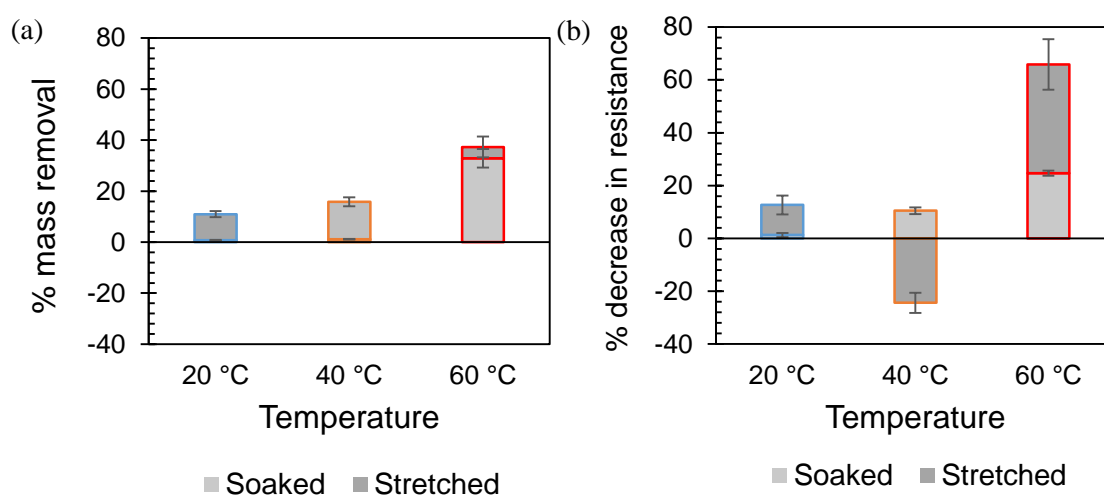
Due to the very different elastic properties of the fabrics it was decided that the work done on the fabric would be equal, but that the force and distance would be altered. For polyester, a stretch of 10 N over 2 cm was used, and for cotton a stretch of 40 N over 0.5 cm was used. Both fabrics were stretched 100 times over 10 minutes.

7.2.1. Polyester

7.2.1.1. Effect of Temperature

Mass, colour and resistance measurements

Results for removal of sebum from polyester after stretching are presented in Figure 7.39. Overall, it can be seen that stretching doesn't offer much of a benefit over soaking, and under some conditions actually leads to less removal. At 60 °C removal as judged by mass or colour change shows no real benefit, whereas the resistance of the fabric is significantly decreased by stretching. This suggests that as the fabric is stretched the surfactant can penetrate the pores more effectively leading to removal of the sebum. Some benefit is seen when the fabric is stretched at 20 °C on all measures of cleaning. Removal by stretching at 40 °C is significantly less than removal at 20 °C. At 40 °C removal is higher for soaked fabric than stretched on all measures of cleaning. For resistance, after stretching this has actually increased and is more resistant than the soiled fabric. It is thought that the stretching of the fabric encourages the molten sebum to occupy the pores of the fabric, and when the fabric contracts the sebum is trapped in the pore as it is not fully liquefied.



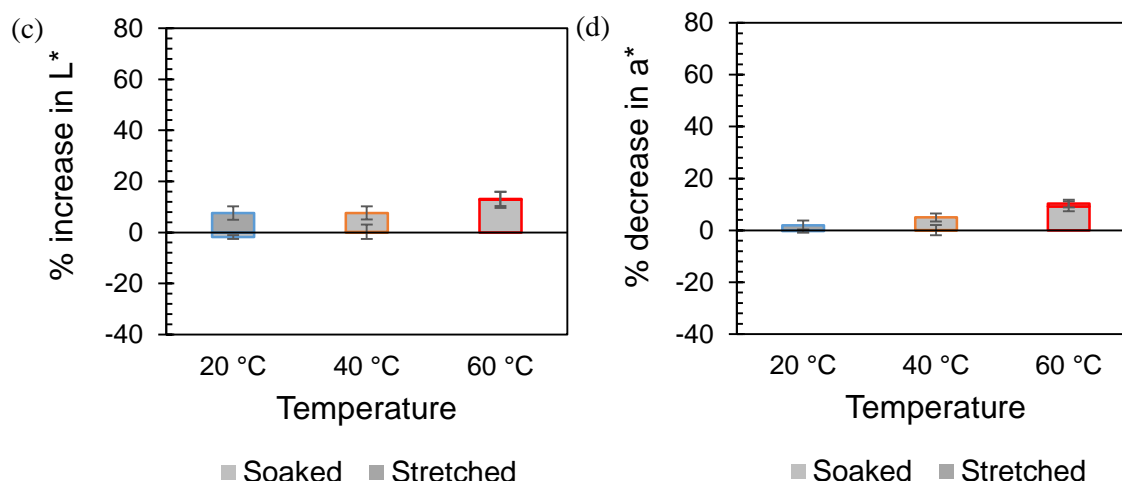


Figure 7.39. Effect of temperature on stretching of polyester soiled with sebum. Surfactant was used at a concentration of 2 x CMC. Cleaning is measured by (a) % mass removal, (b) % decrease in resistance, (c) % increase in L^* and (d) % decrease in a^* . The error bars represent \pm one standard deviation for three fabrics. Five measurements were taken from each fabric for colour and resistance.

Colour of top and underside of fabric

When the topside and underside of the fabric are considered, as in Figure 7.40, it can be seen that at 60 °C removal is very similar from both sides, and is not too dissimilar for 20 °C. This is not the case for 40 °C, where removal from the underside of the fabric is much less than the topside, and in fact the underside is darker and redder than the soiled polyester. This suggests some sebum has travelled from the topside to the underside of the fabric, which fits with the theory above that it is now occupying the pores.

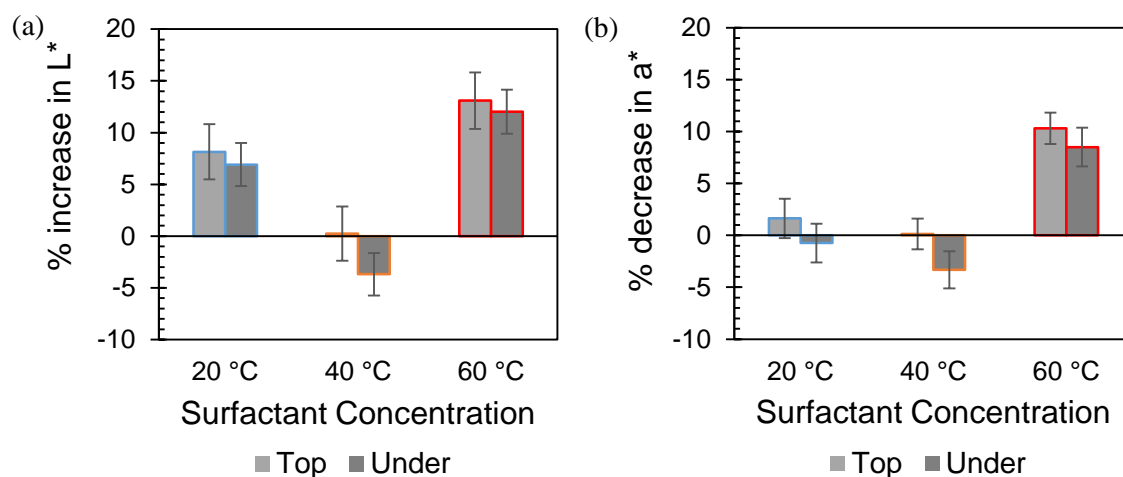


Figure 7.40. Comparison of the colour of the top and underside of polyester soiled with sebum cleaned using the stretching rig at 20 °C, 40 °C and 60 °C with surfactant at a concentration of 2 x CMC. Colour is measured as (a) L* and (b) a*. The error bars represent \pm one standard deviation for three fabrics. Five measurements were taken from each fabric.

Mass per unit area

Figure 7.41 shows the mass per unit area of the fabrics after stretching. It can be seen that removal is maximised at 60 °C, as has been found previously. Removal is least at 40 °C, and the central strip of the soiled area is actually higher in mass than the soiled fabric. This suggests some sebum has moved into this area from the two surrounding soiled strips. This confirms that the sebum is mobile on the fabric surface. It can also be seen that the mass per unit area of the unsoiled area of the fabric has only reduced at the highest temperature, which is due to stretching the fabric. Once the fabric is released from the stretching rig it is unable to return to its original shape as it has stretched beyond its elasticity limit.

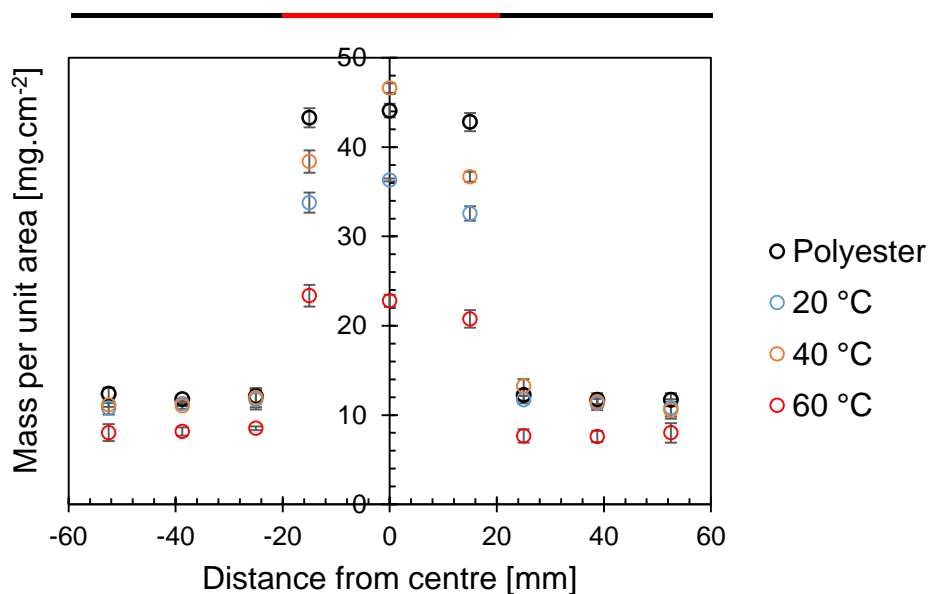


Figure 7.41. Mass per unit area of polyester soiled with sebum cleaned using the stretching rig at 20 °C, 40 °C and 60 °C with surfactant at a concentration of 2 x CMC. The error bars represent \pm one standard deviation for three fabrics.

FTIR

FTIR results, presented in Figure 7.42, show that all polyester fabrics appear similar in chemical make up to the soiled fabric. Polyester peaks, such as those at 1240 and 1090 cm^{-1} , are masked by the sebum under all conditions. At 40 °C the underside peak at 2880 and 2850 cm^{-1} appears to have increased in size, in line with results presented previously. The same peak on the topside stretched with 60 °C has reduced in size.

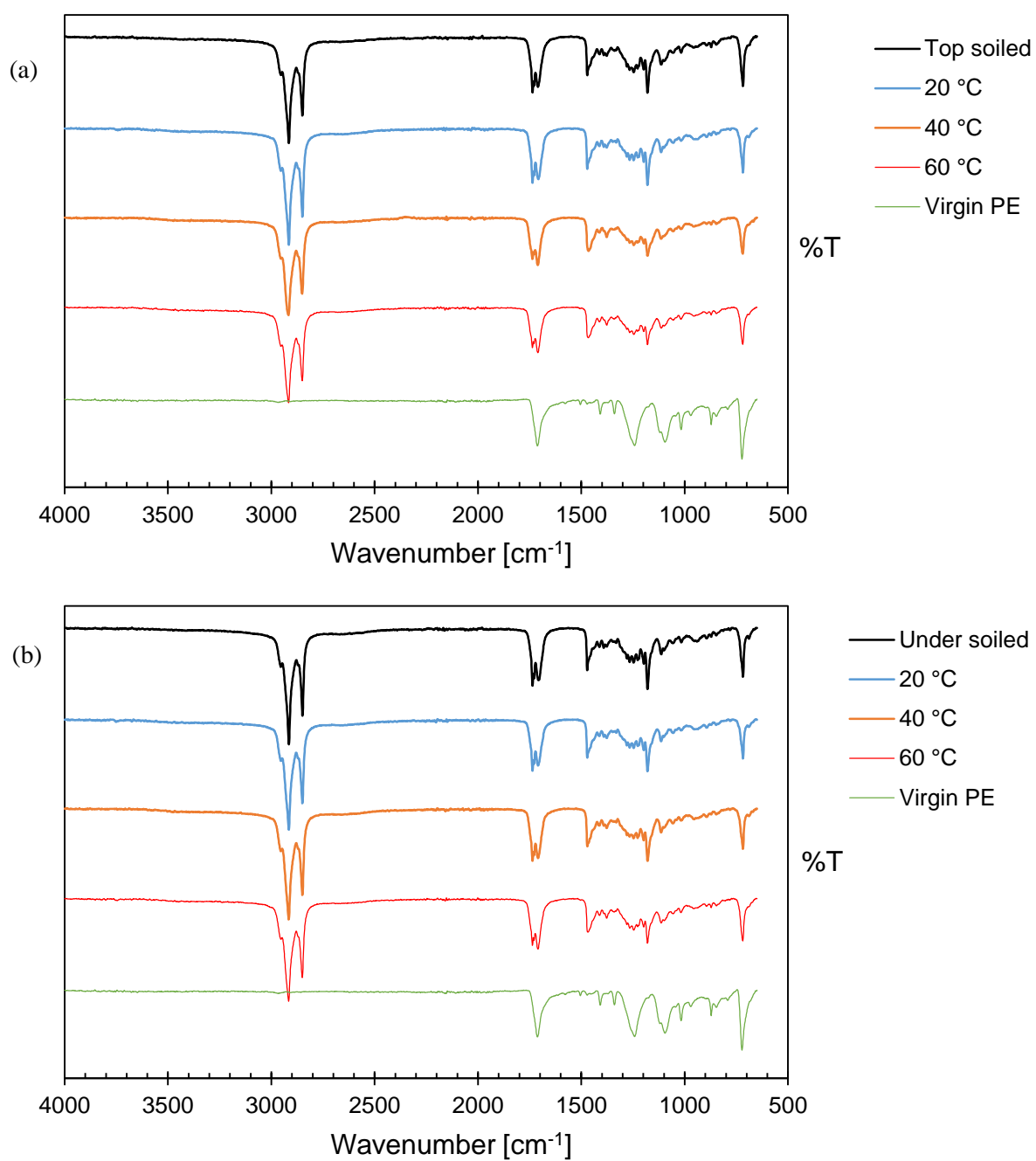
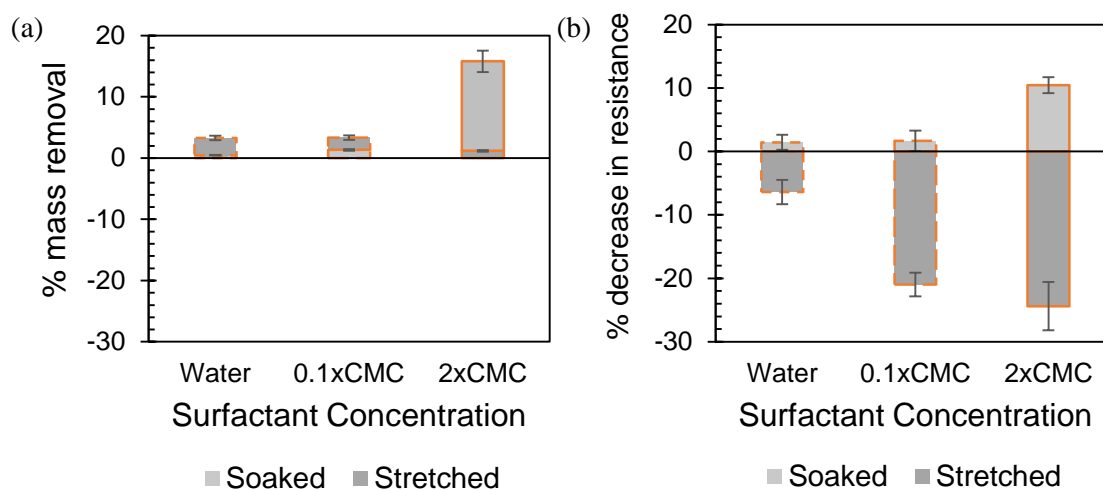


Figure 7.42. FTIR of polyester soiled with sebum cleaned using the stretching rig at 20 °C, 40 °C and 60 °C with surfactant at a concentration of 2 x CMC. This is compared to soiled and virgin polyester for both the (a) top and (b) underside of the fabric.

7.2.1.2. Effect of surfactant concentration at 40 °C

Mass, colour and resistance measurements

Removal at 40 °C with stretching is low for all conditions. Colour changes are less than soaking alone, as is mass removal when twice the CMC is used. Removal is lowest when twice the CMC is used. It is suspected that the surfactant solubilises the sebum allowing it to move into the pores of the fabric when it's stretched. When the fabric then contracts the soil is trapped in the pore and removal is then not possible. For all three surfactant concentrations resistance increases beyond that observed for soiled polyester. Again this likely to be due to the trapping of sebum in the pores.



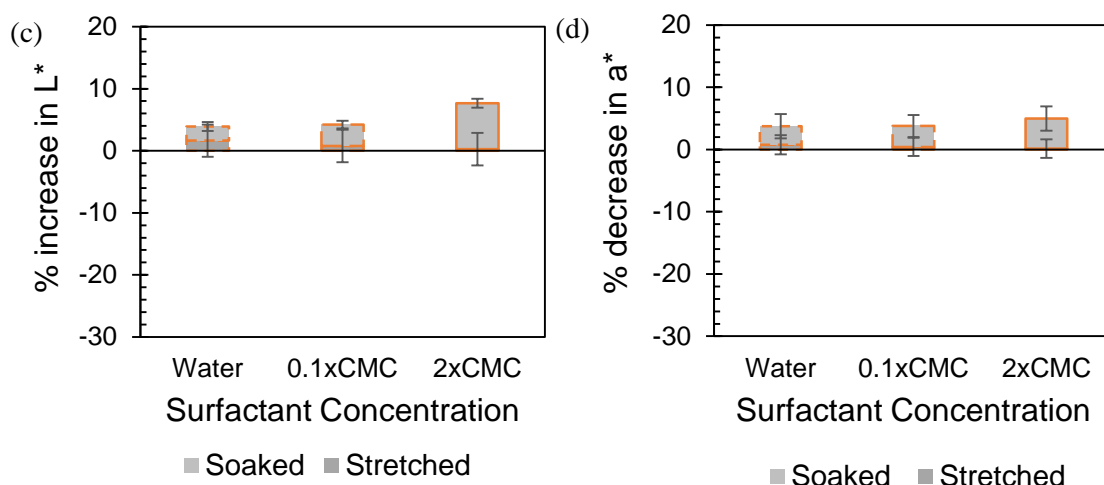


Figure 7.43. Effect of surfactant concentration on stretching at 40 °C for polyester soiled with sebum. Cleaning is measured by (a) % mass removal, (b) % decrease in resistance, (c) % increase in L^* and (d) % decrease in a^* . The error bars represent \pm one standard deviation for three fabrics. Five measurements were taken from each fabric for colour and resistance.

Colour of top and underside of fabric

Figure 7.44 shows the colour of the topside and underside of fabrics stretched in 40 °C surfactant solution. It can be seen that changes in colour are very low. The underside of the fabric is found to be darker and redder than the soiled polyester. This supports the mechanism suggested above that sebum, aided by surfactant, moves into the pores of the fabric and becomes trapped increasing the amount of sebum observed on the underside of the fabric.

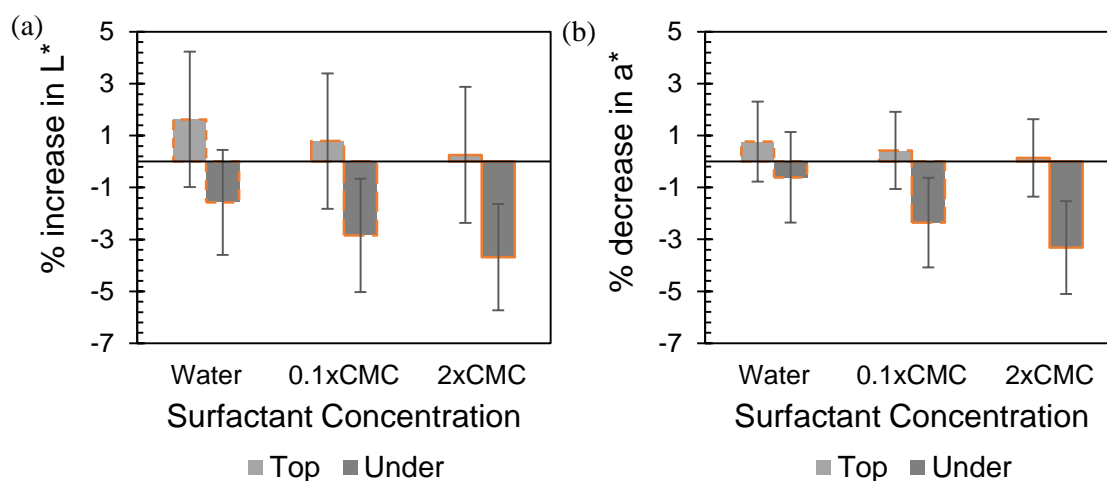


Figure 7.44. Comparison of the colour of the top and underside of polyester soiled with sebum cleaned using the stretching rig at 40 °C with water and surfactant at a concentration of 0.1 x and 2 x CMC. Colour is measured as (a) L^* and (b) a^* . The error bars represent \pm one standard deviation for three fabrics. Five measurements were taken from each fabric.

Mass per unit area

Mass per unit area measurements, presented in Figure 7.45, show that mass of the central strip actually increases when surfactant is used, whereas the mass of the two surrounding strips decreases, confirming that sebum is able to move around the fabric. No difference in mass is seen for the unsoiled area of fabric.

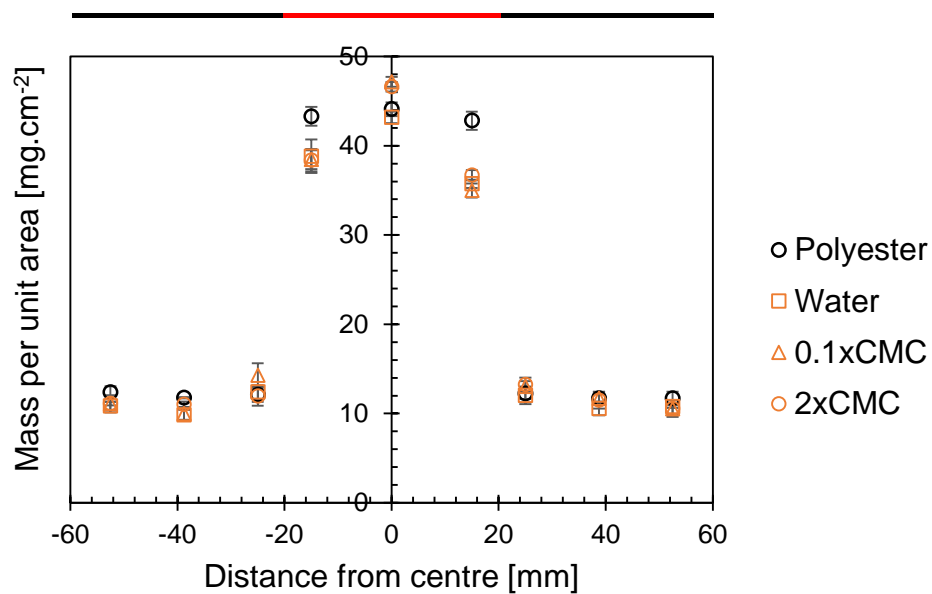


Figure 7.45. Mass per unit area of polyester soiled with sebum cleaned using the stretching rig at 40 °C with water and surfactant at a concentration of 0.1 x and 2 x CMC. The error bars represent \pm one standard deviation for three fabrics.

FTIR

FTIR spectra, presented in Figure 7.46, show all three samples are very similar to the soiled fabric, which is to be expected as mass removal is very low. Polyester peaks 1715, 1240 and 1090 cm^{-1} are masked by the sebum as FTIR only looks at the surface.

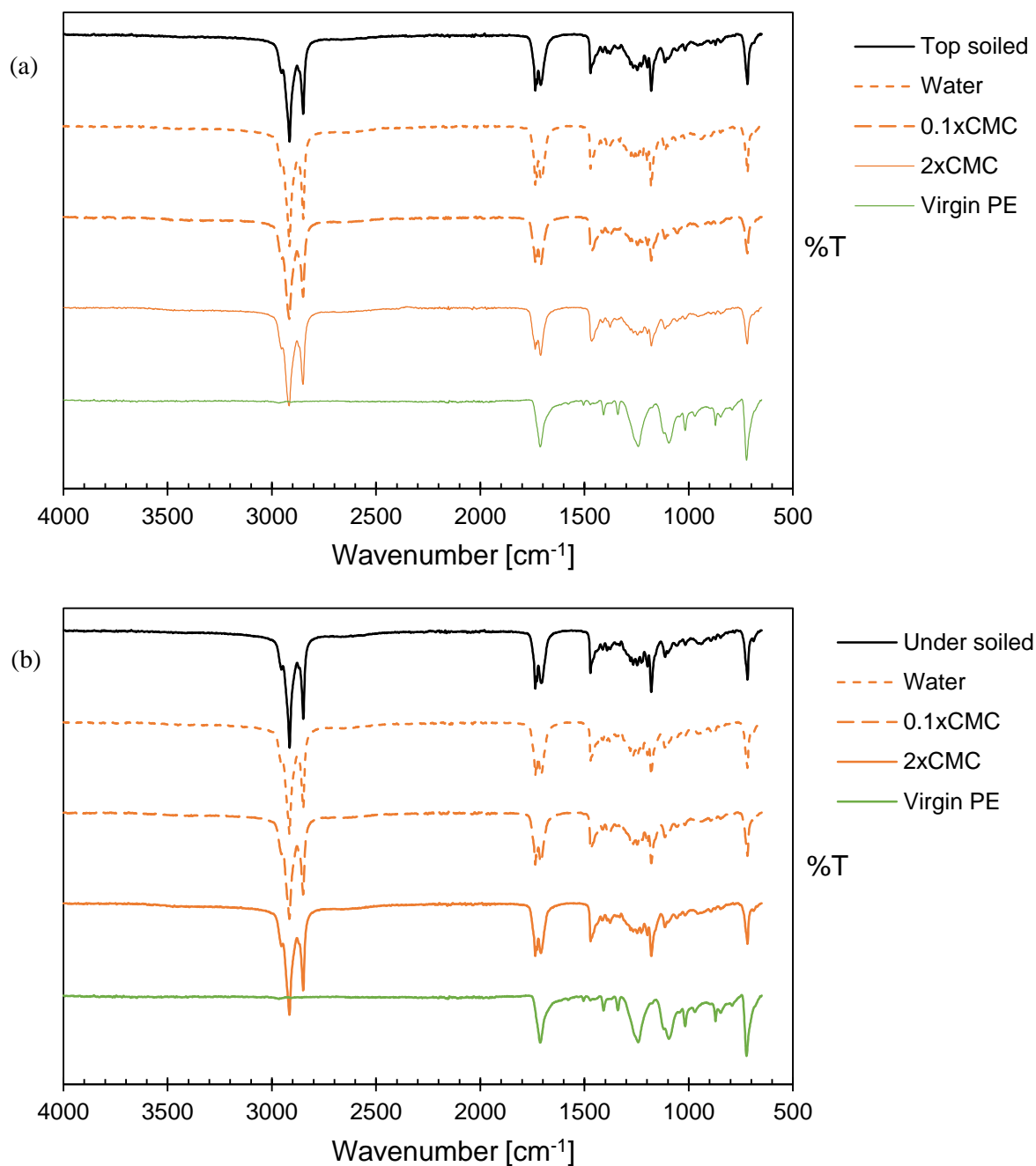


Figure 7.46. FTIR of polyester soiled with sebum cleaned using the stretching rig at 40 °C with water and surfactant at a concentration of 0.1 x and 2 x CMC. This is compared to soiled and virgin polyester for both the (a) top and (b) underside of the fabric.

SEM

SEM images of these fabrics were obtained to further aid explanation of the results. All three samples appear fairly similar, with similar numbers of uncoated threads and pores. When compared to soiled polyester in Figure 4.21 the sebum in these images appears less grainy, particularly on the x100

image. This suggests that the molten sebum has homogenised as it has moved to occupy the pores of the fabric.

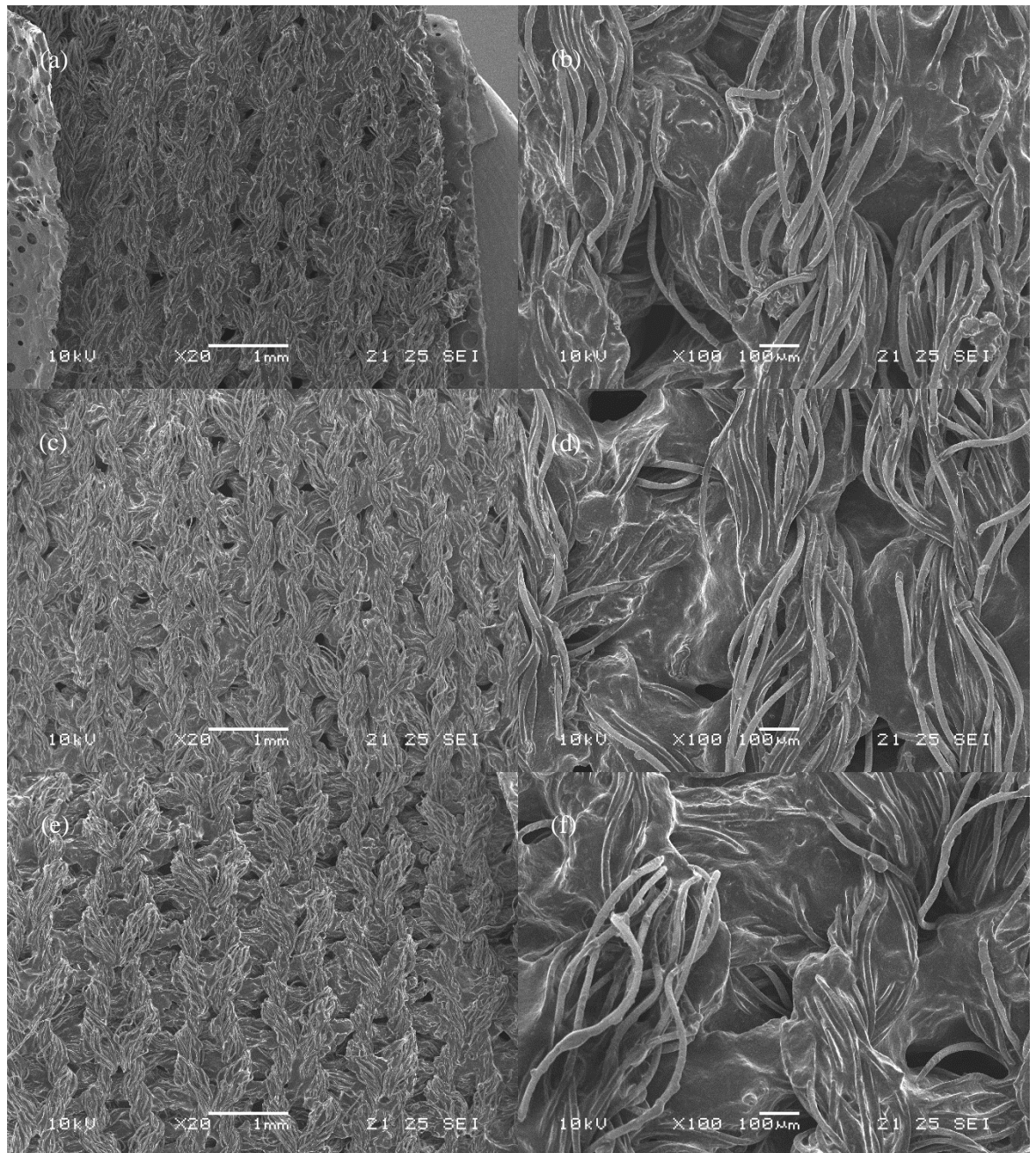


Figure 7.47. SEM images of soiled polyester stretched in 40 °C wash solution with (a, b) water, (c, d) 0.1 x CMC surfactant solution and (e, f) 2 x CMC surfactant solution at (a, c, e) x20, (b, d, f) x100 magnifications.

SEM images were also obtained for the cross section of the fabrics, as shown in Figure 7.48. Once again it can be seen that the grainy texture of the sebum has reduced when compared to Figure 4.22.

It also appears that sebum has moved into the pores where fibres are running parallel to the image. Fibres perpendicular to the image are relatively clean so sebum is unable to penetrate these yarns.

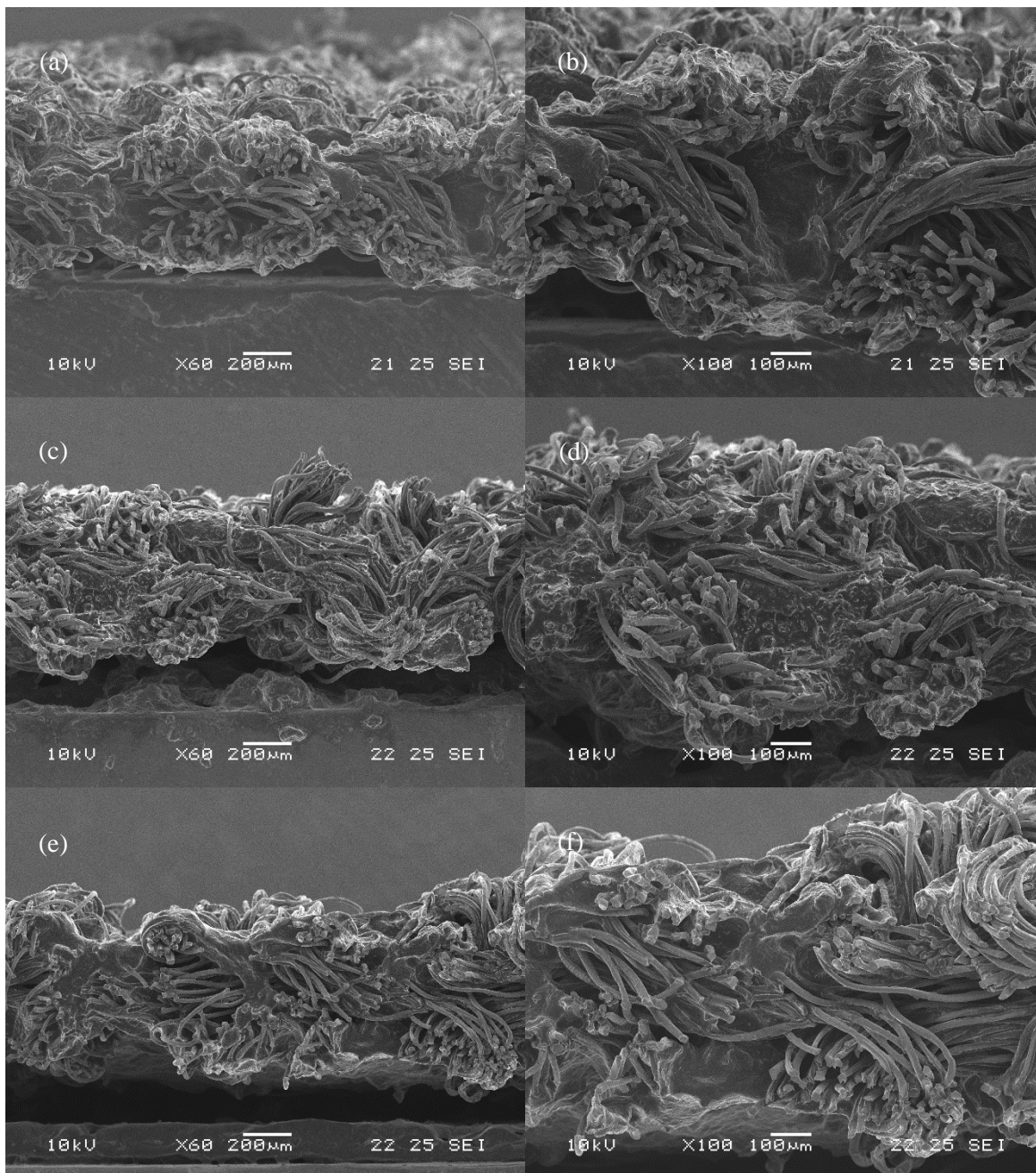
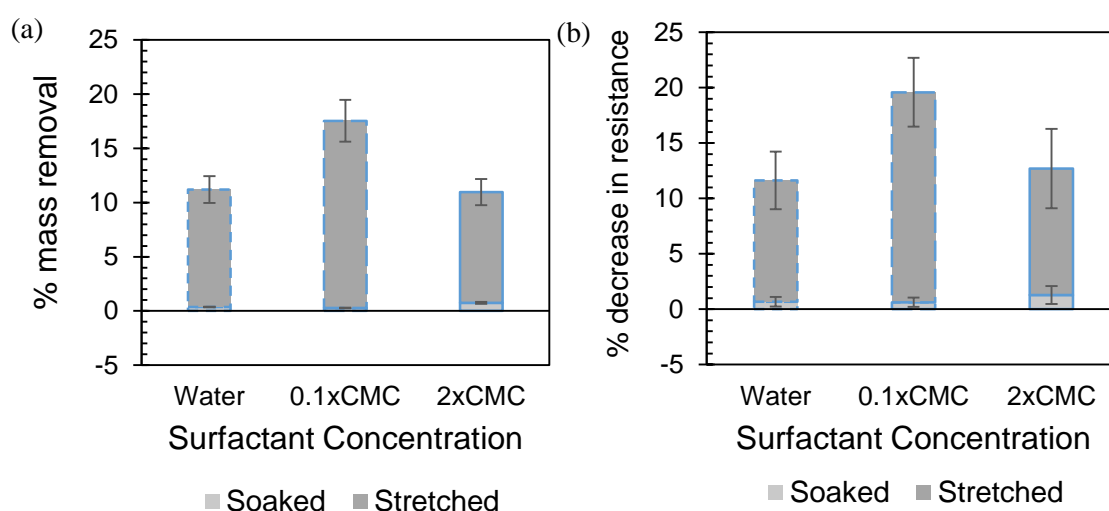


Figure 7.48. SEM images of the cross section of soiled polyester stretched in 40 °C wash solution with (a, b) water, (c, d) 0.1 x CMC surfactant solution and (e, f) 2 x CMC surfactant solution at (a, c, e) x60, (b, d, f) x100 magnifications.

7.2.1.3. Effect of surfactant concentration at 20 °C

Mass, colour and resistance measurements

Figure 7.49 shows removal of sebum when fabrics are stretched in 20 °C wash solution. Removal is much higher when fabrics are stretched compared to soaking alone. Interestingly, removal is highest when a low amount of surfactant is used, and there is very little difference between wash solution consisting of water or twice the CMC of surfactant solution. The reason for this may be that at twice the CMC the surfactant solubilises the sebum allowing it to penetrate the fabric and become trapped in to the pores leading to less removal overall. This mechanism occurs to a lesser extent at this temperature so some removal is still seen, unlike at 40 °C.



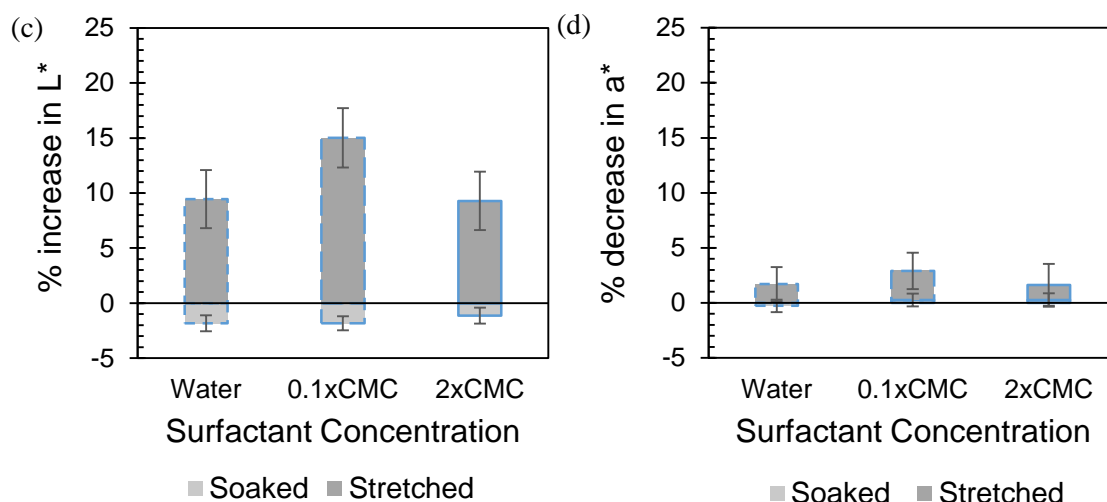


Figure 7.49. Effect of surfactant concentration on stretching at 20 °C for polyester soiled with sebum. Cleaning is measured by (a) % mass removal, (b) % decrease in resistance, (c) % increase in L^* and (d) % decrease in a^* . The error bars represent \pm one standard deviation for three fabrics. Five measurements were taken from each fabric for colour and resistance.

Colour of top and underside of fabric

Figure 7.50 shows removal from the topside and underside of the fabric. It can be seen that removal from the underside of the fabric is significantly less than the topside, and the redness of the underside actually increases after stretching. This supports the mechanisms that sebum moves from the topside of the fabric to the pores and hence can be seen on the underside of the fabric.

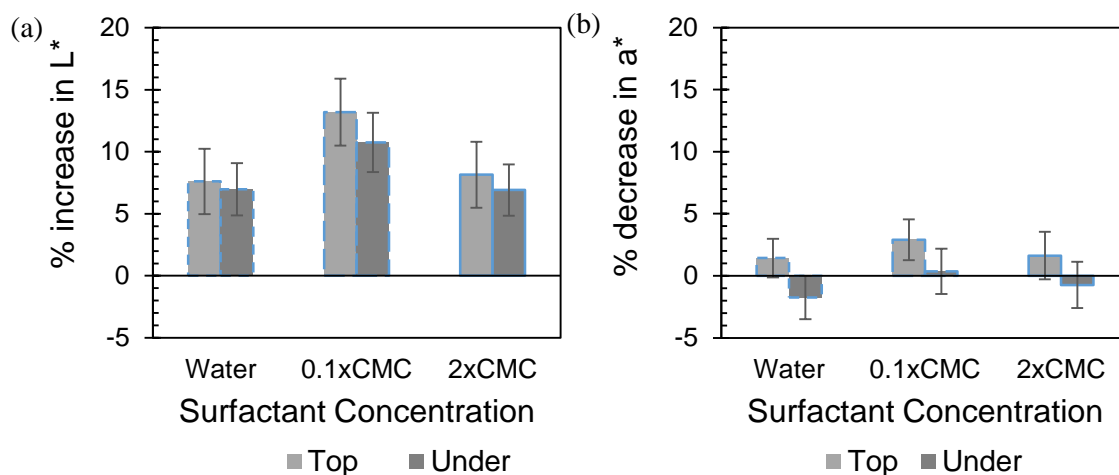


Figure 7.50. Comparison of the colour of the top and underside of polyester soiled with sebum cleaned using the stretching rig at 20 °C with water and surfactant at a concentration of 0.1 x and 2 x CMC. Colour is measured as (a) L* and (b) a*. The error bars represent \pm one standard deviation for three fabrics. Five measurements were taken from each fabric.

Mass per unit area

Mass per unit area results for fabrics stretched in 20 °C wash solution are presented in Figure 7.51.

Results show that removal is higher with 0.1 times the CMC, as found earlier. Removal is similar for twice the CMC and water. Some decrease in the mass per unit area of the unsoiled area of fabric is observed indicating that stretching has gone beyond the elasticity point of the fabric and it has not returned to its original shape.

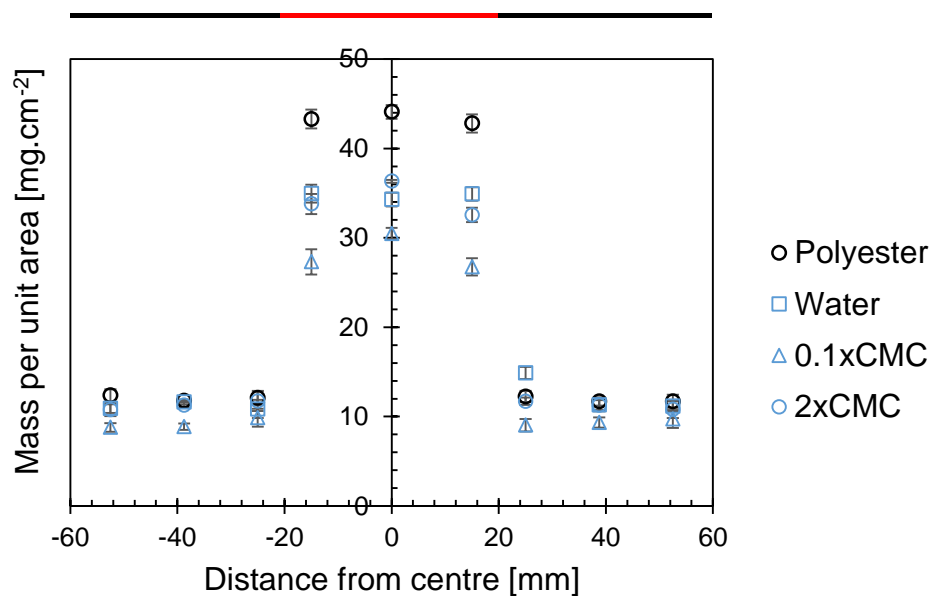
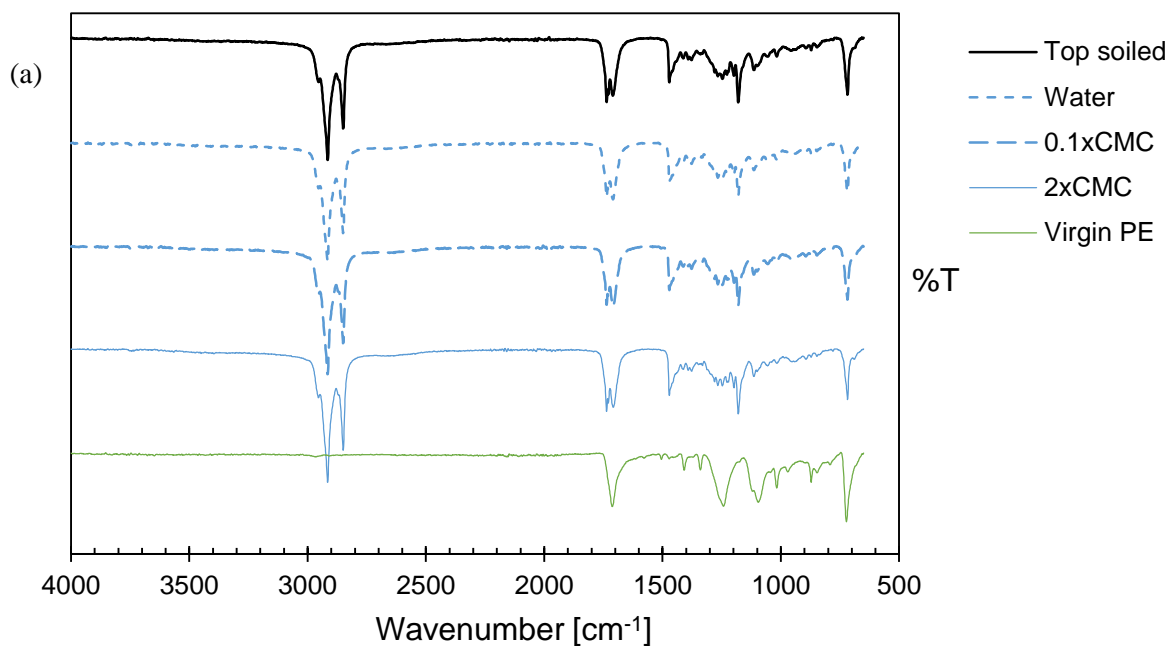


Figure 7.51. Mass per unit area of polyester soiled with sebum cleaned using the stretching rig at 20 °C with water and surfactant at a concentration of 0.1 x and 2 x CMC. The error bars represent \pm one standard deviation for three fabrics.

FTIR

FTIR results, shown in Figure 7.52, show very little difference between all three fabrics, and when compared to soiled polyester. Again, it can be seen that polyester peaks are masked by the sebum.



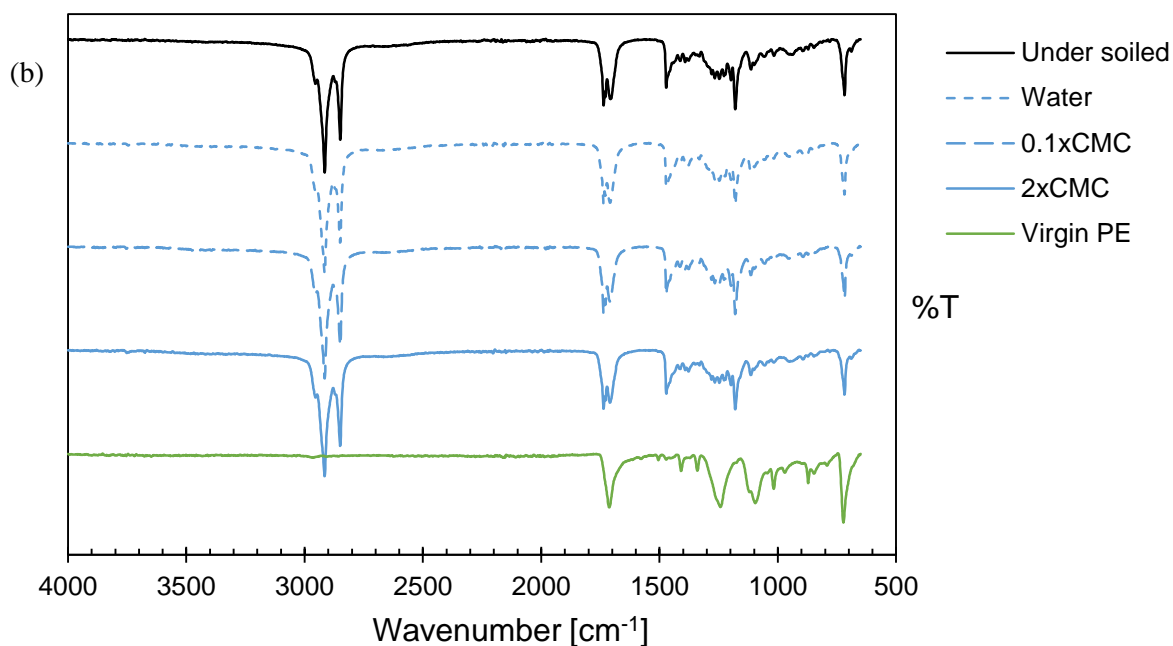


Figure 7.52. FTIR of polyester soiled with sebum cleaned using the stretching rig at 20 °C with water and surfactant at a concentration of 0.1 x and 2 x CMC. This is compared to soiled and virgin polyester for both the (a) top and (b) underside of the fabric.

7.2.2. Cotton

7.2.2.1. Effect of Temperature

Mass, colour and resistance measurements

Figure 7.53 shows removal for cotton stretched in wash solution with twice the CMC of surfactant at three different temperatures. It can be seen that, unlike polyester, stretching increases removal of sebum at all temperatures, although the additional removal is low. The greatest increase in removal is seen at 60 °C, indicating that removal from cotton when the fabric is stretched is dependent on how liquefied the sebum is. The greatest increase for all samples is seen in the change in resistance, which is explained by the fact that stretching changes the shape of the pore making the sebum within the pores more accessible to the wash solution.

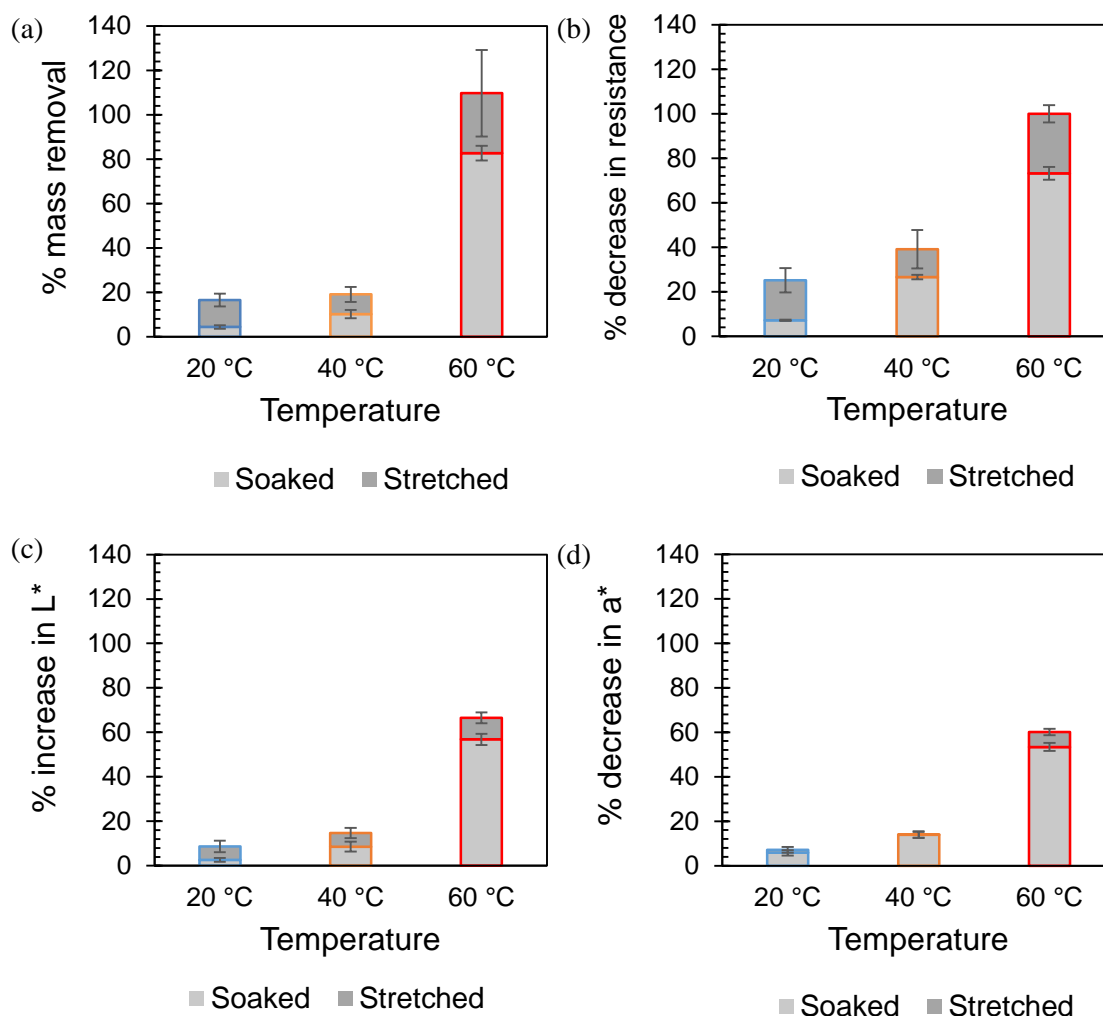


Figure 7.53. Effect of temperature on stretching of cotton soiled with sebum. Surfactant was used at a concentration of 2 x CMC. Cleaning is measured by (a) % mass removal, (b) % decrease in resistance, (c) % increase in L^* and (d) % decrease in a^* . The error bars represent \pm one standard deviation for three fabrics. Five measurements were taken from each fabric for colour and resistance.

Colour of top and underside of fabric

Figure 7.54 compares the colour of the top and underside of the cotton stretched in wash solution with twice the CMC of surfactant at three different temperatures. Removal from the underside is lower, and in some cases the fabric actually appears more dirty. At 20 °C and 40 °C, the surfactant has mobilised the sebum, but not removed it from the underside. At 60 °C this may occur, but is masked by overall removal.

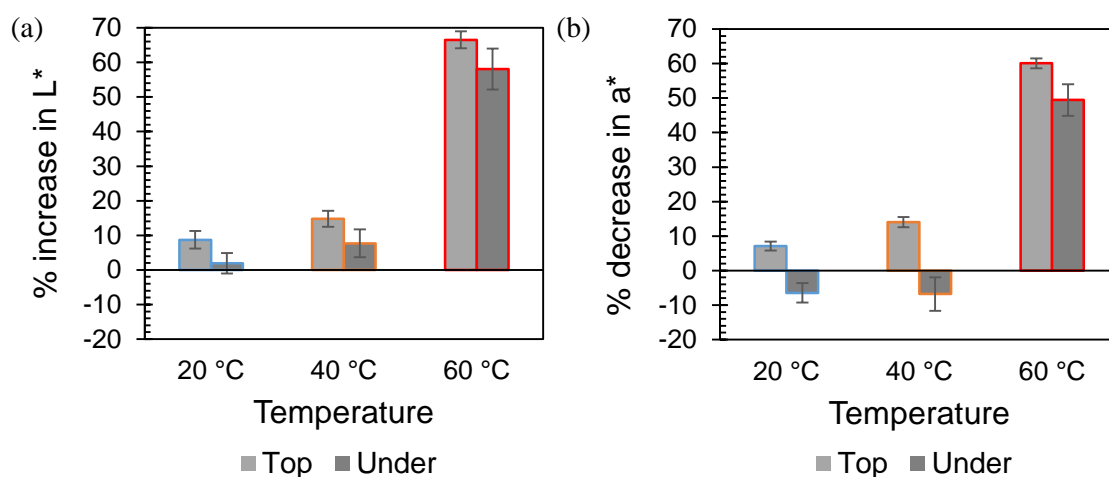


Figure 7.54. Comparison of the colour of the top and underside of cotton soiled with sebum cleaned using the stretching rig at 20 °C, 40 °C and 60 °C with surfactant at a concentration of 2 x CMC. Colour is measured as (a) L^* and (b) a^* . The error bars represent \pm one standard deviation for three fabrics. Five measurements were taken from each fabric.

Mass per unit area

Mass per unit area results, presented in Figure 7.55, show that removal at 60 °C decreases the mass of the soiled strip to approximately the same mass as virgin cotton. Removal is much lower at the lower temperatures. The mass of the unsoiled area does not change significantly indicating stretching has not altered the fabric itself, and no spreading of soil is observed.

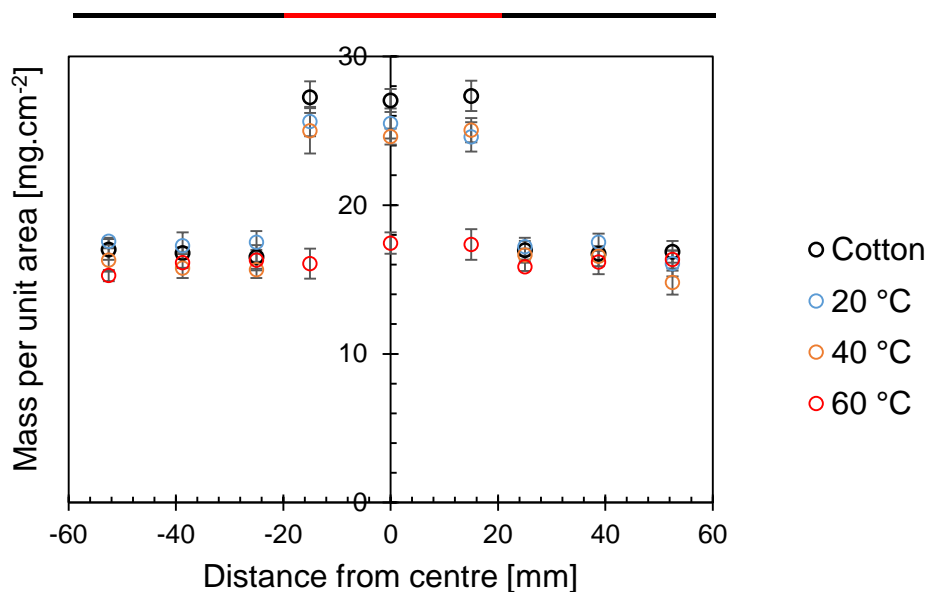


Figure 7.55. Mass per unit area of cotton soiled with sebum cleaned using the stretching rig at 20 °C, 40 °C and 60 °C with surfactant at a concentration of 2 x CMC. The error bars represent \pm one standard deviation for three fabrics.

FTIR

Figure 7.56 shows FTIR spectra of the three stretched cotton fabrics, and compares them to soiled and virgin cotton. It can be seen that the cotton peak at 3300 cm⁻¹ is masked on the topside of the fabric at the lower temperature, but becomes more visible when 60 °C used. The sebum peaks at 2880 and 2850 cm⁻¹ have not reduced in size at the lower temperatures, but are much smaller at 60 °C.

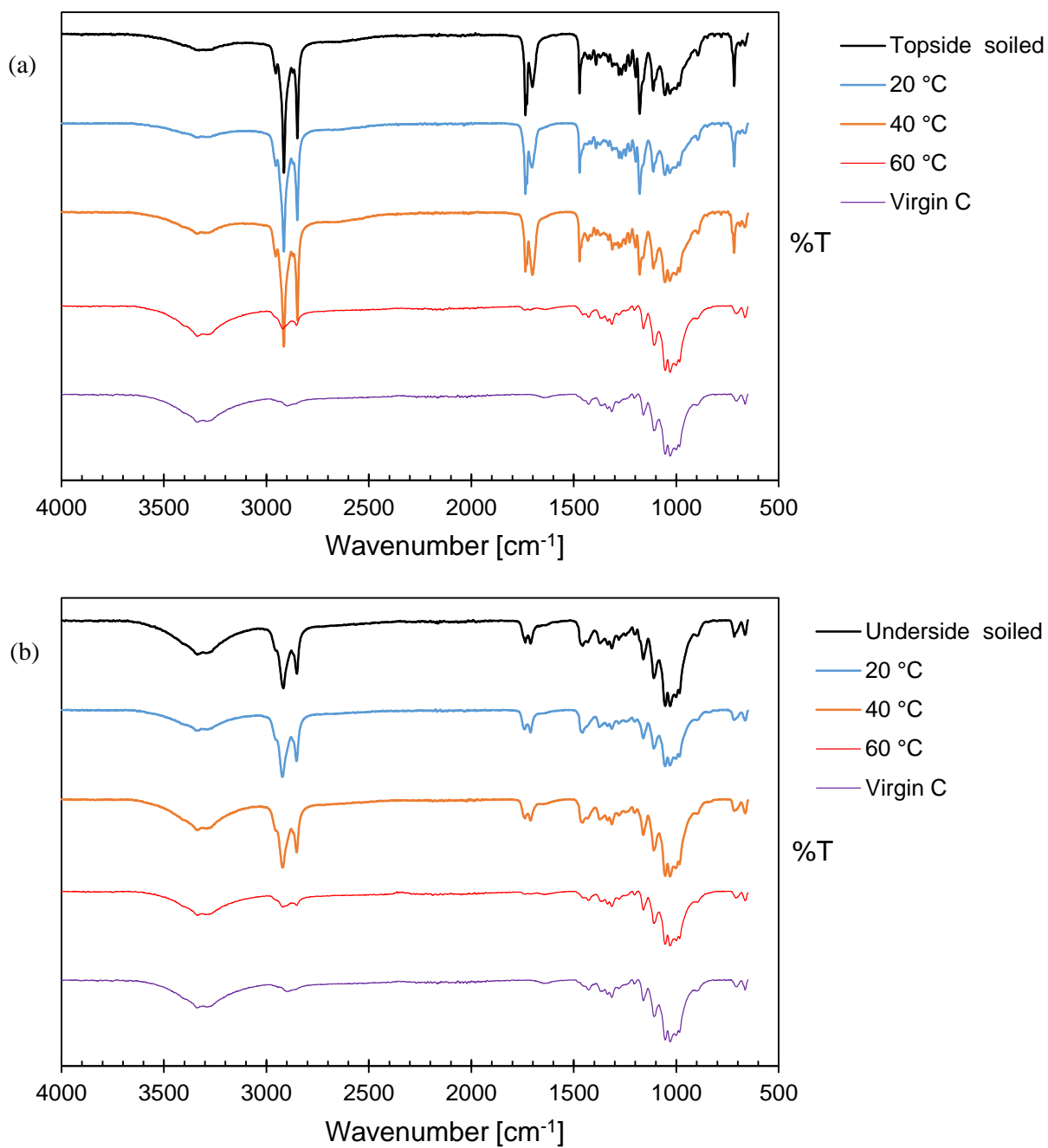
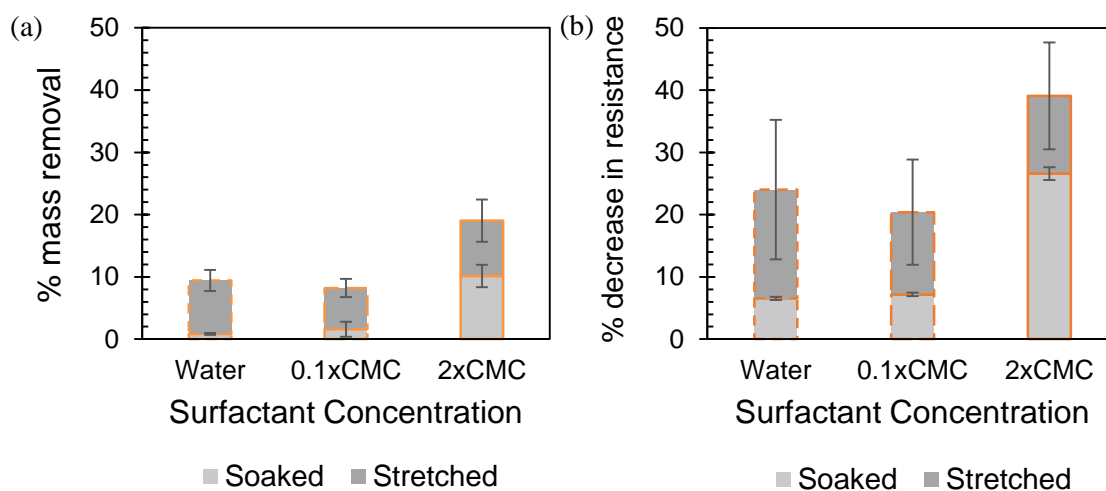


Figure 7.56. FTIR of cotton soiled with sebum cleaned using the stretching rig at 20 °C, 40 °C and 60 °C with surfactant at a concentration of 2 x CMC. This is compared to soiled and virgin cotton for both the (a) top and (b) underside of the fabric.

7.2.2.2. Effect of surfactant concentration at 40 °C

Mass, colour and resistance measurement

At 40 °C removal remains highest when twice the CMC of the surfactant is used, as shown in Figure 7.57. This is as expected as the surfactant aids removal of the soil. However, when 0.1 times the CMC of the surfactant is used cleaning is reduced when compared to water alone, particularly when colour change is considered. The difference between water and the lower concentration of surfactant is not as great suggesting the difference in removal is mainly due to removal from the surface of the fabric, as the water is not able to penetrate the pores to aid removal here.



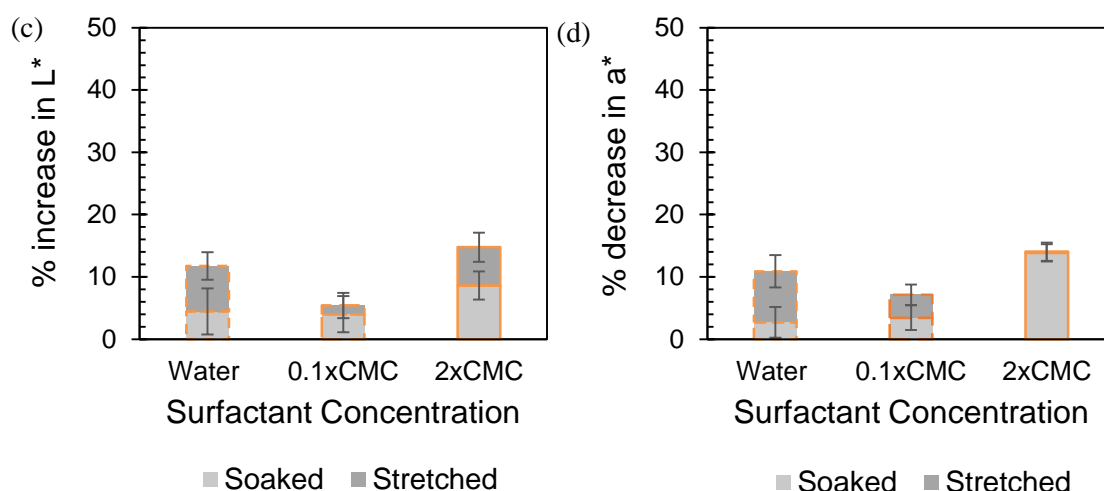


Figure 7.57. Effect of surfactant concentration on stretching at 40 °C for cotton soiled with sebum. Cleaning is measured by (a) % mass removal, (b) % decrease in resistance, (c) % increase in L* and (d) % decrease in a*. The error bars represent \pm one standard deviation for three fabrics. Five measurements were taken from each fabric for colour and resistance.

Colour of top and underside of fabric

Figure 7.58 shows that removal from the underside of the fabric is significantly less than removal from the top side, and, in some case, the underside of the fabric has become dirtier. This suggests sebum has been transported from the topside to the less soiled underside, suggesting the wash solutions at 40 °C are able to mobilise the soil, but not completely remove it. This is observed particularly when 0.1 times the CMC of the surfactant is used indicating the surfactant aids this mobilization. At 2 times the CMC the concentration of surfactant is then high enough to remove the soil to a greater extent.

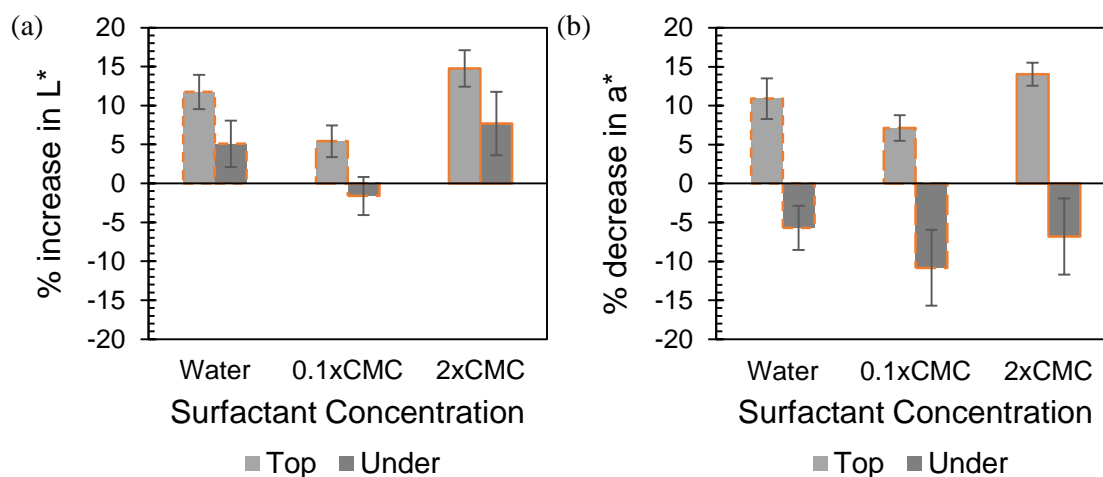


Figure 7.58. Comparison of the colour of the top and underside of cotton soiled with sebum cleaned using the stretching rig at 40 °C with water and surfactant at a concentration of 0.1 x and 2 x CMC. Colour is measured as (a) L* and (b) a*. The error bars represent \pm one standard deviation for three fabrics. Five measurements were taken from each fabric.

Mass per unit area

Mass per unit area measurements, as shown in Figure 7.59, show a small amount of removal from the soiled strip for all samples, with the most removal when twice the CMC is used. This is in line with previous results in this section. The mass of the surrounding fabric remains unchanged which indicates the sebum does not spread into this area and the fabric is not stretched to a point that the mass per unit area is changed.

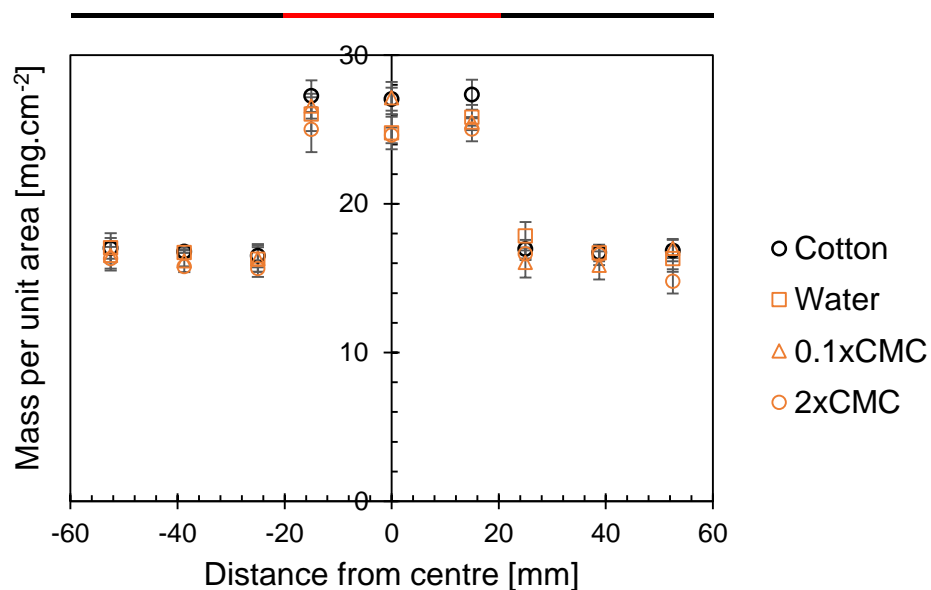


Figure 7.59. Mass per unit area of cotton soiled with sebum cleaned using the stretching rig at 40 °C with water and surfactant at a concentration of 0.1 x and 2 x CMC. The error bars represent \pm one standard deviation for three fabrics.

FTIR

FTIR spectra for these conditions as well as virgin and soiled cotton are presented in Figure 7.60. It can be seen that on the topside all washed fabrics are very similar to soiled cotton, and there are no major differences between the three concentrations of surfactant. On the underside of the fabric for soiled cotton the cotton peaks at 3300 and 3270 cm^{-1} are not masked, whereas on the samples washed with water and the lower concentration of surfactant there is some masking of these peaks. This is in line with results presented earlier in this section.

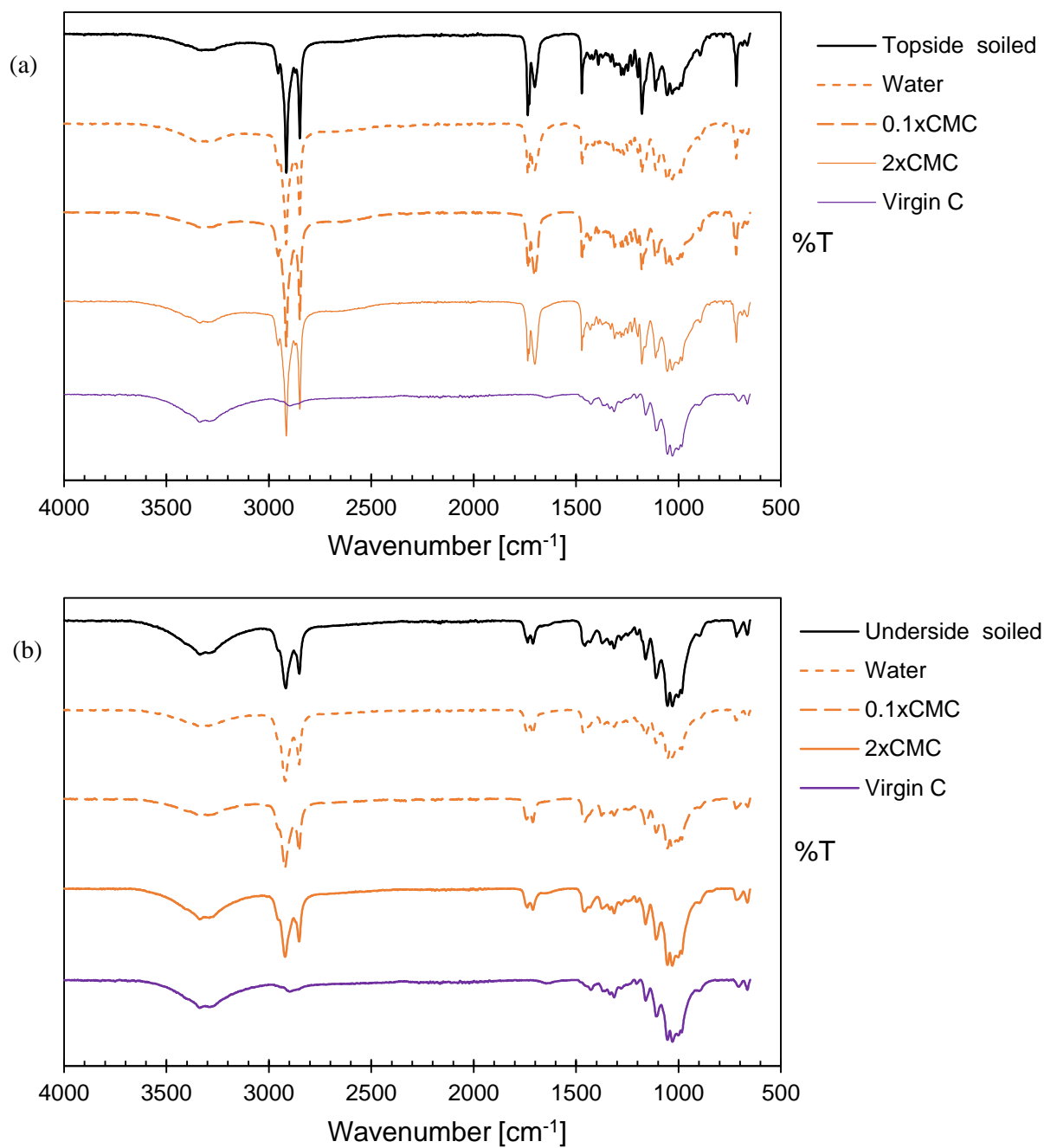
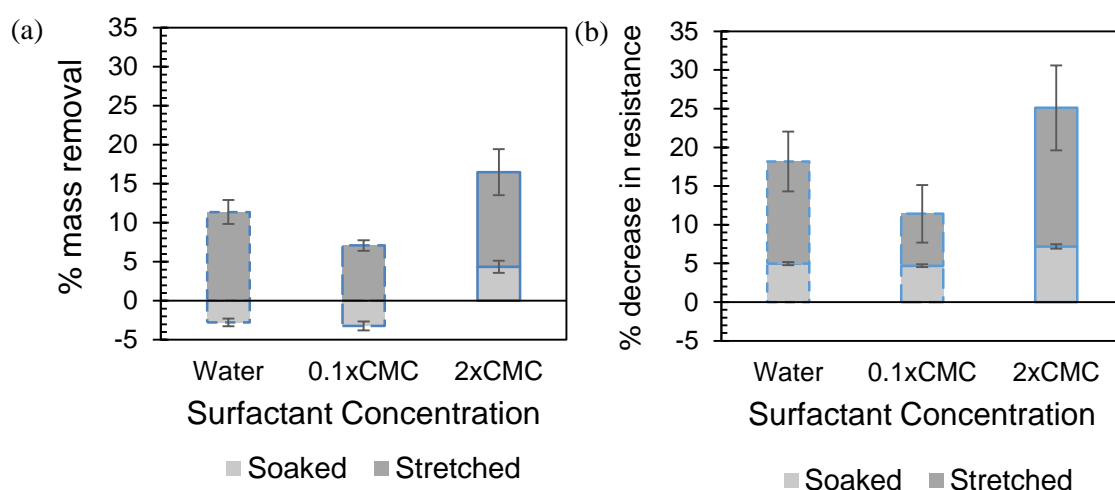


Figure 7.60. FTIR of cotton soiled with sebum cleaned using the stretching rig at 40 °C with water and surfactant at a concentration of 0.1 x and 2 x CMC. This is compared to soiled and virgin cotton for both the (a) top and (b) underside of the fabric.

7.2.2.3. Effect of surfactant concentration at 20 °C

Mass, colour and resistance measurements

Under all conditions at 20 °C stretching increases removal of sebum, as shown in Figure 7.61. Removal is highest when twice the CMC is used, as expected. Interestingly, the same trend observed in section 7.2.2.2 is also observed at 20 °C, that surfactant at 0.1 times the CMC decreases cleaning when compared to water alone. At 20 °C a bigger decrease is seen when resistance is considered, which indicates that at the lower concentration of surfactant, the surfactant aids mobilisation of the sebum on the fabric but doesn't fully remove it. Resistance results suggests some of this sebum remains in the pores, partially blocking them. The action of stretching allows water to remove some sebum from the pores which would not otherwise have been accessible to the water.



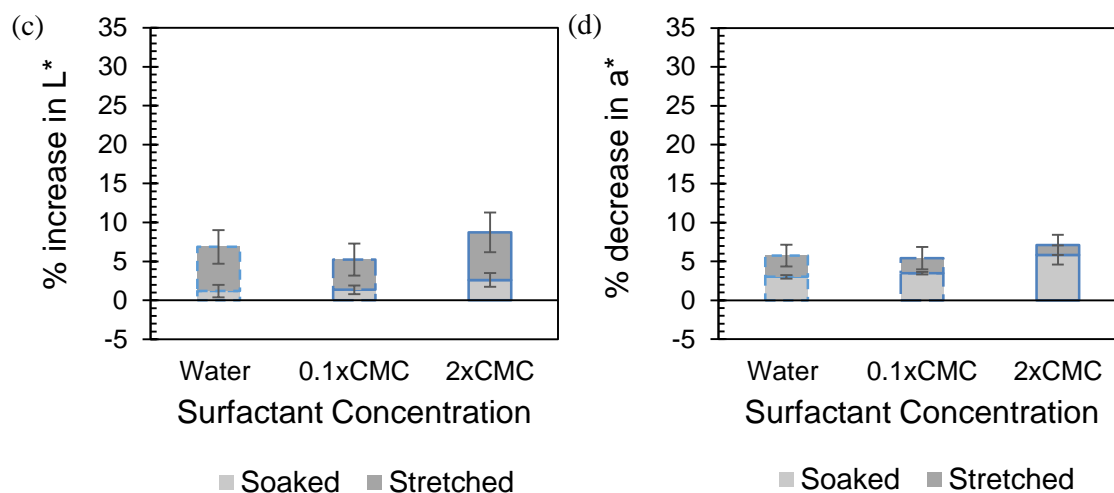


Figure 7.61. Effect of surfactant concentration on stretching at 20 °C for cotton soiled with sebum. Cleaning is measured by (a) % mass removal, (b) % decrease in resistance, (c) % increase in L^* and (d) % decrease in a^* . The error bars represent \pm one standard deviation for three fabrics. Five measurements were taken from each fabric for colour and resistance.

Colour of top and underside of fabric

Figure 7.62 compares the colour change on the topside and underside of the fabric. We can see that in most cases the underside of the fabric is actually dirtier after stretching, whereas the topside has been cleaned. This suggests that the stretching action has shifted the sebum from the more concentrated top surface to the less dirty underside.

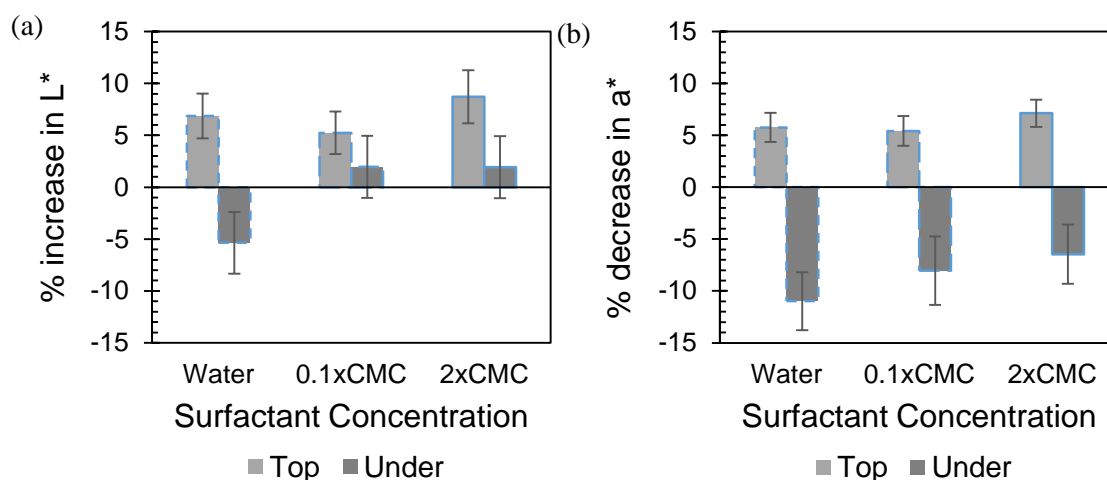


Figure 7.62. Comparison of the colour of the top and underside of cotton soiled with sebum cleaned using the stretching rig at 20 °C with water and surfactant at a concentration of 0.1 x and 2 x CMC. Colour is measured as (a) L^* and (b) a^* . The error bars represent \pm one standard deviation for three fabrics. Five measurements were taken from each fabric.

Mass per unit area

Mass per unit area results, shown in Figure 7.63, show very little removal from the central soiled area, and no change in mass for the surrounding area. This indicates stretching hasn't changed the geometry of the fabric, and the sebum has not spread from the soiled area.

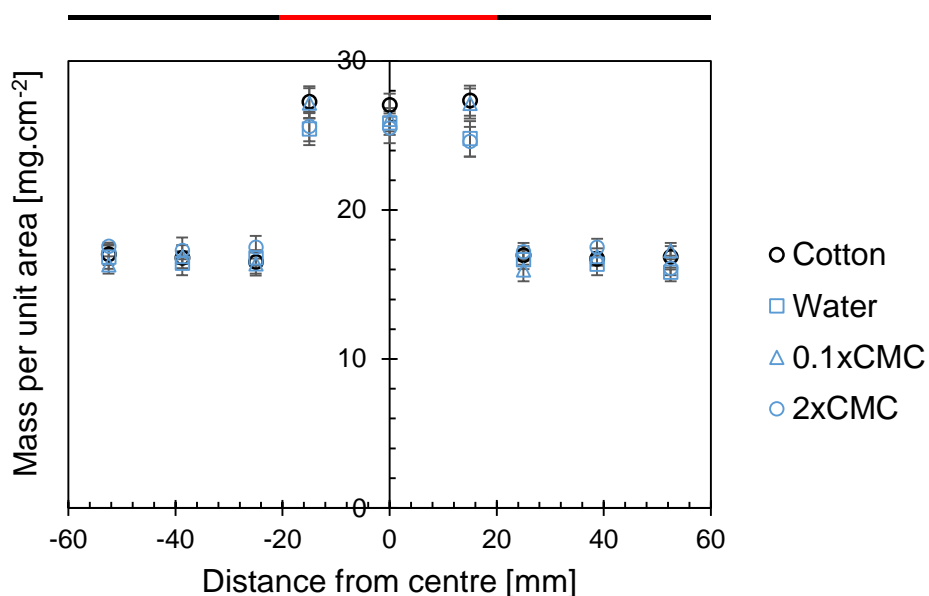


Figure 7.63. Mass per unit area of cotton soiled with sebum cleaned using the stretching rig at 20 °C with water and surfactant at a concentration of 0.1 x and 2 x CMC. The error bars represent \pm one standard deviation for three fabrics.

FTIR

FTIR spectra, presented in Figure 7.64, show that all washed samples are very similar to soiled cotton. This is to be expected as removal is low at this temperature and FTIR is only able to analyse the surface, and fits with previous results presented in this section.

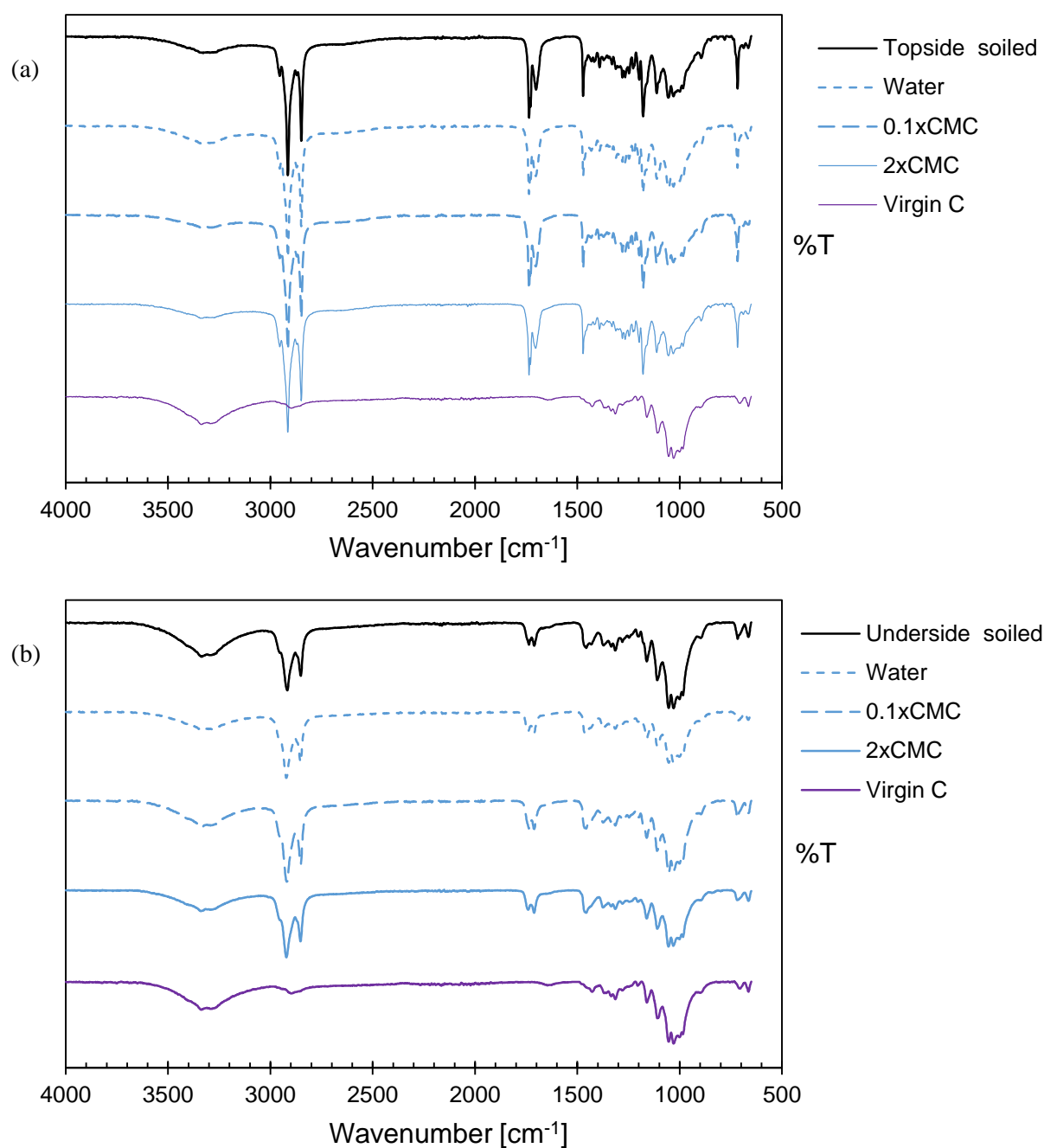


Figure 7.64. FTIR of cotton soiled with sebum cleaned using the stretching rig at 20 °C with water and surfactant at a concentration of 0.1 x and 2 x CMC. This is compared to soiled and virgin cotton for both the (a) top and (b) underside of the fabric.

7.2.3. Discussion on stretching

When the temperature of wash solution is investigated for stretching polyester, it can be seen that the results are not as intuitive. At 20 °C there is a significant benefit to stretching the fabric, and at 60

°C a small benefit is observed over soaking alone. However, at 40 °C, cleaning is worse than when the fabric is soaked and is more similar to the original soiled fabric. In the case of resistance change, this is found to be worse than original soiled fabric. A possible mechanism for this could be that the temperature allows the sebum to become molten, without being fully liquefied, and as such is mobile on the surface of the fabric. As the fabric is stretched the sebum transfers into the pores and remains here when the fabric returns to its original size. This effect is not seen on cotton, where stretching gives a small benefit at all temperatures on all measures of cleaning. It is suspected that this difference is linked to the high level of elasticity of the polyester allowing large changes in the size of the pores, which is not possible with cotton.

When the effect of surfactant is considered at 20 °C for polyester, increased removal of sebum is observed when 0.1 times the CMC of the surfactant is used, when compared to water or twice the CMC. It is suspected that the high concentration of surfactant aids mobilisation of the sebum on the fabric, which then becomes trapped in the pores of the elastic material rather than being fully removed. Again, this effect is not observed on cotton, where the use of surfactant at the lower level leads to less sebum removal than when water alone is used. This trend is observed at both 20 °C and 40 °C. One possible mechanism could be entrapment of solubilised sebum when low concentrations of surfactant are used, whereas mechanisms such as solubilisation and emulsification can fully remove the sebum when the higher concentration is used. These differences appear to be due to the different structures and elasticities of the fabrics.

Chapter 8: Comparing the effect of chemical actions, hydrodynamics and mechanical actions on cleaning

In this chapter removal by the different methods – chemical action, hydrodynamics and mechanical actions - are compared across all conditions for both polyester and cotton.

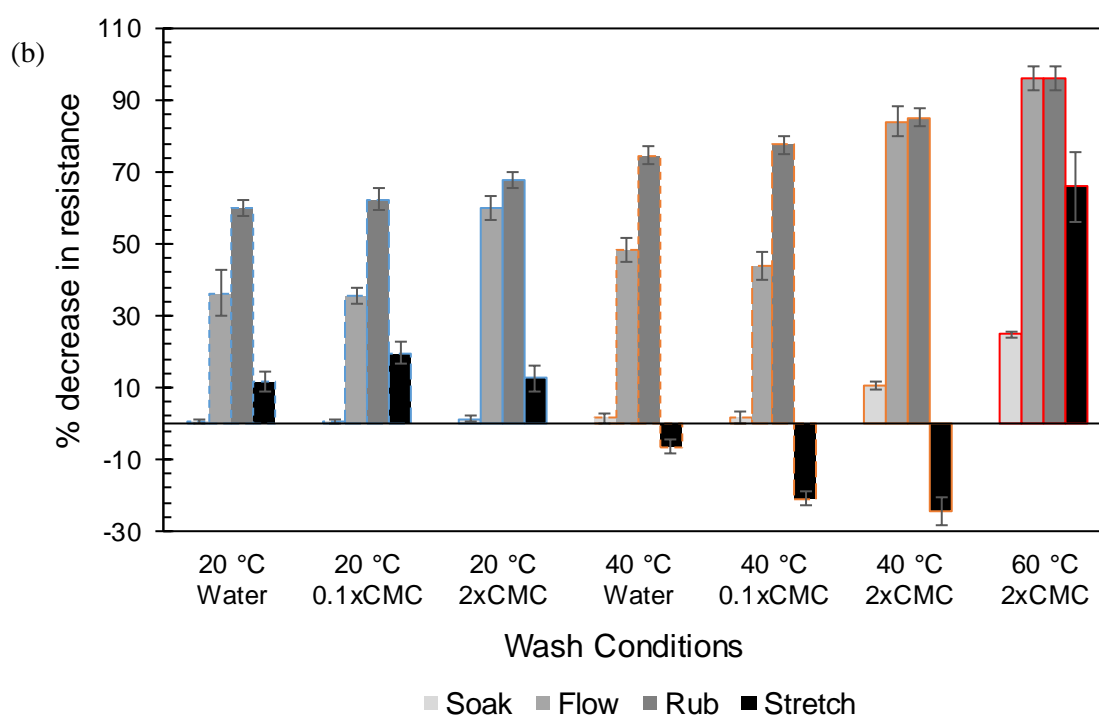
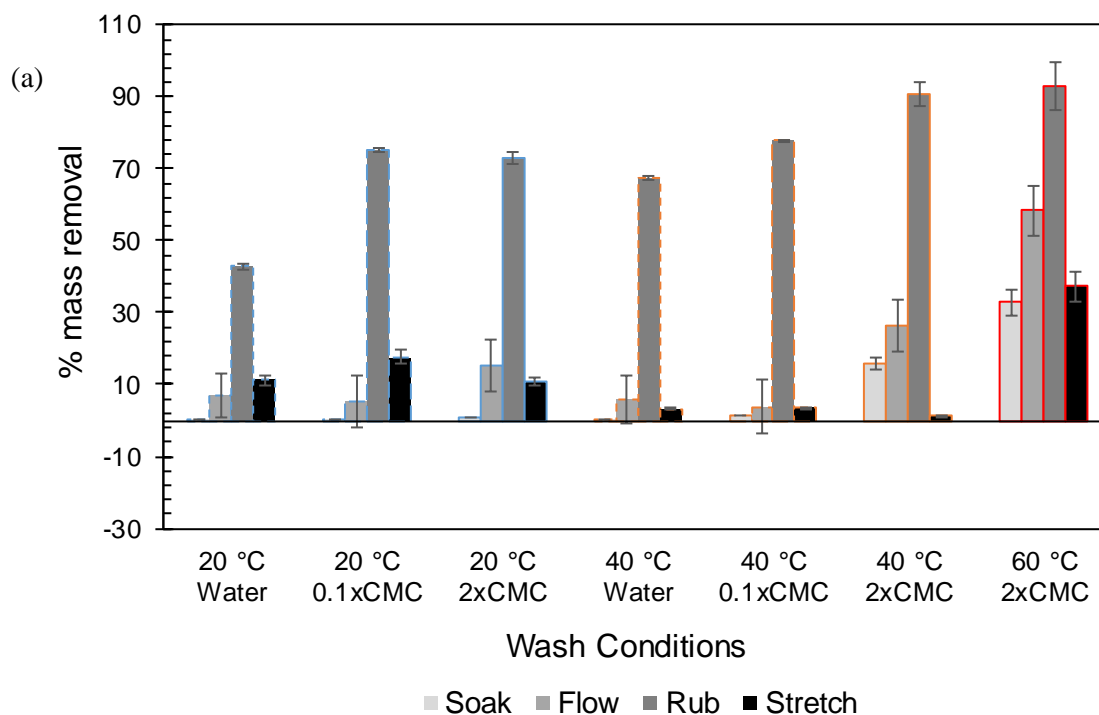
8.1. Polyester

Removal of sebum from polyester by soaking, flow, rubbing and stretching is presented in Figure 8.1. For percentage mass removal and percentage decrease in resistance, rubbing shows the highest removal over all temperatures and surfactant concentrations, from 42.8 to 92.9 % removal for mass, and 59.7 to 96.1 % decrease in resistance. This is due to the magnitude of the downward force from the rubbing blade on the fabric surface removing the surface layer of sebum as it moves across it. The force from the rubbing blade will also flatten the fibres, and manipulations of the fabric as the blade moves across the surface are both likely to change the pore sizes forcing sebum trapped within them to be moved to the surface and subsequently removed by the rubbing blade. Under most conditions rubbing shows the best improvement in colour, except at 60 °C. At this temperature removal is highest for flow, where the increase in L^* is 72.4 %, compared to 47.0 % for rubbing under the same conditions. The same trend is observed with a^* . The action of flow is thought to better aid removal of sebum from within the pores of the fabric as the wash solution imparts shear on the sebum, and this force is not present when the fabric is rubbed. The effect is only observed at this temperature, when the sebum is fully liquefied. The shear force only affects removal from the top side of the fabric, where the shear force is imparted, as evidenced by the fact that overall mass removal and decrease in resistance are not as high.

Soaking shows the least removal under most conditions, with mass removal ranging from 0.37 to 32.9 %. This is intuitive as removal would be expected to be greater when an additional force from flow of water or mechanical action were used. It is also thought that some of the sebum will be

trapped within the pores and will not be accessible to the wash solution. However, the exception to this is polyester stretched in 40 °C wash solution with either high or low concentrations of surfactant, where removal is found to be lower, as discussed in Section 7.2.1.2.

Under all conditions, a larger decrease in resistance was found when flow was used to remove sebum from polyester compared to stretching. For flow, the decrease in resistance was between 35.5 and 96.1 %, whereas for stretching the maximum decrease was 65 %, and some samples increased resistance when compared to the soiled fabric. This indicates greater cleaning within the pores of the fabric, allowing water to flow more freely through the pores during resistance testing. This is due to the fact that the flow was directed through the pores and shear force of the wash solution on the walls of the pore will remove sebum located there. When mass decrease and colour change are also considered, it was found that on the whole at the lower temperature removal was higher by stretching when compared to flow, whereas at 40 °C and 60 °C the opposite was found. A possible explanation for this could be that at 20 °C the action of stretching causing deformation of the fabric surface, which was able to dislodge more solid sebum. The shear force from the flow of wash solution was not able to remove sebum from the top surface of the fabric.



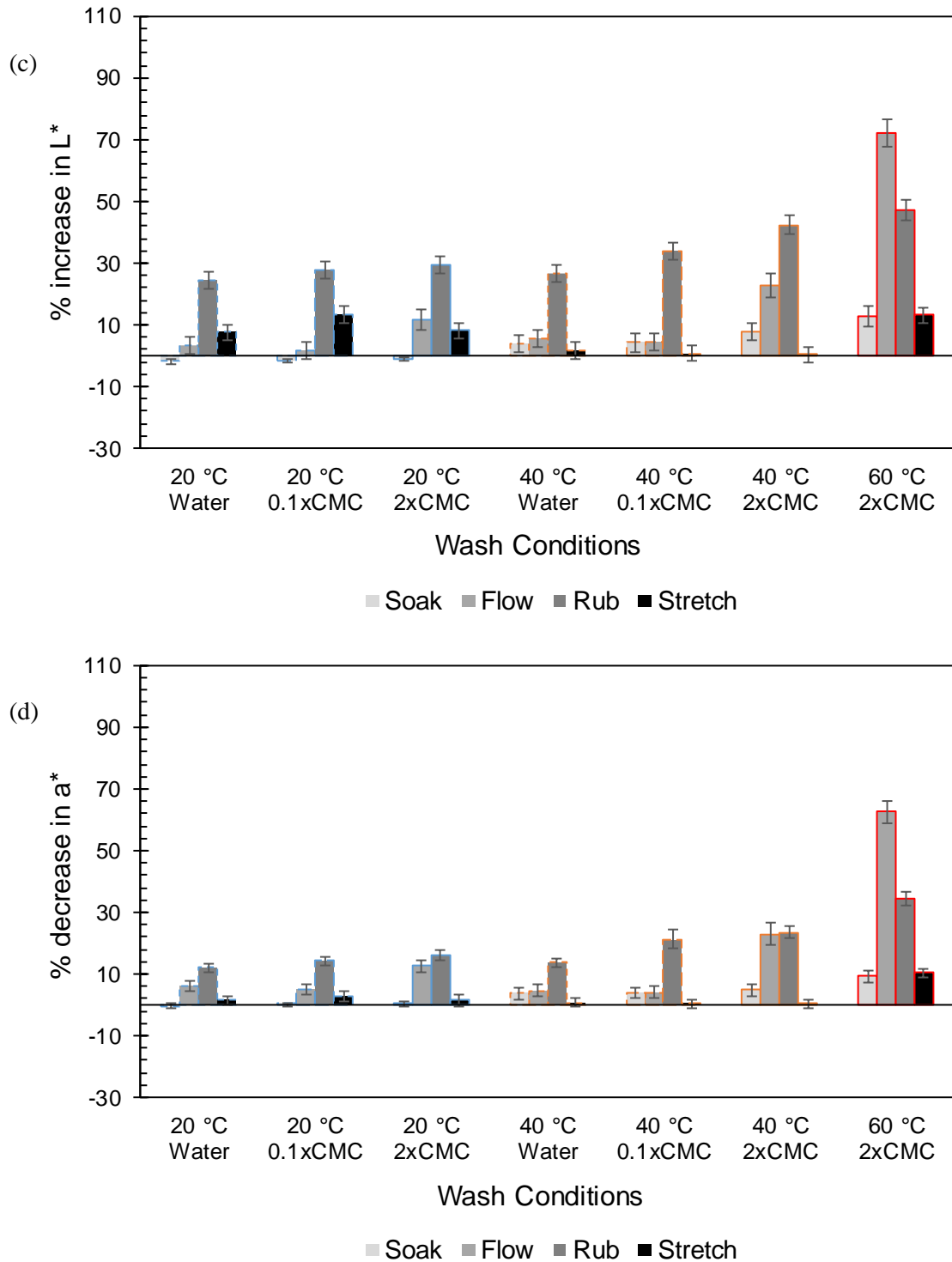


Figure 8.1. Comparing the effect of chemical action, hydrodynamics and mechanical actions on polyester soiled with sebum. Cleaning is measured by (a) % mass removal, (b) % decrease in resistance, (c) % increase in L^* and (d) % decrease in a^* . The error bars represent \pm one standard deviation for three fabrics. Five measurements were taken from each fabric for colour and resistance.

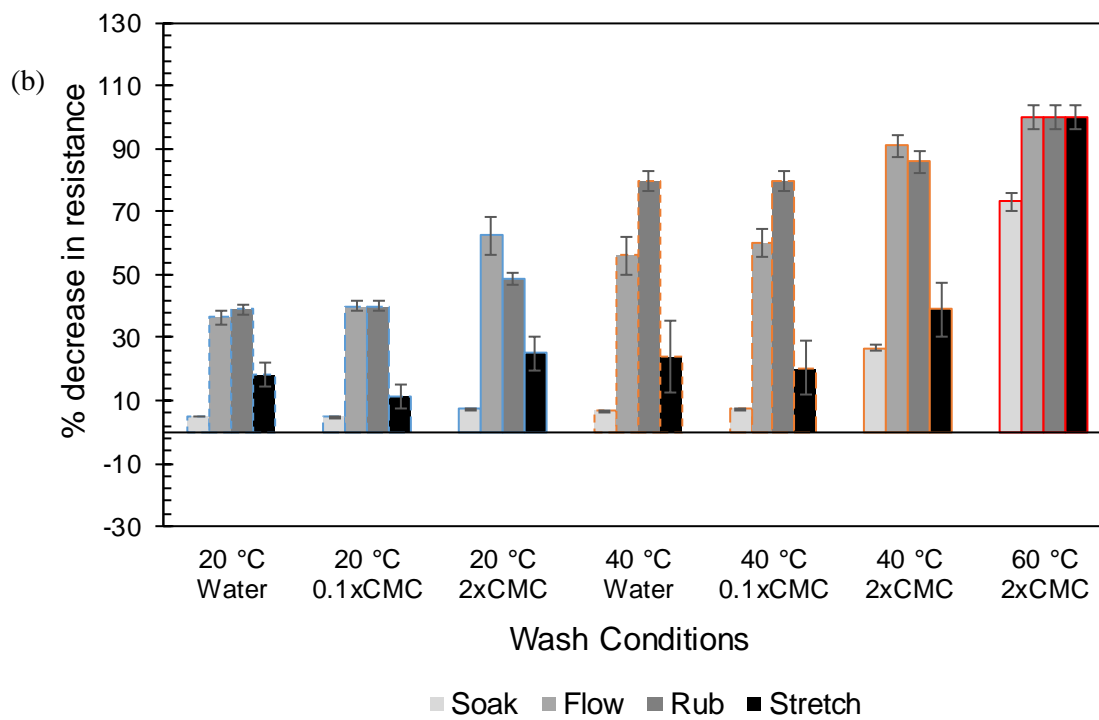
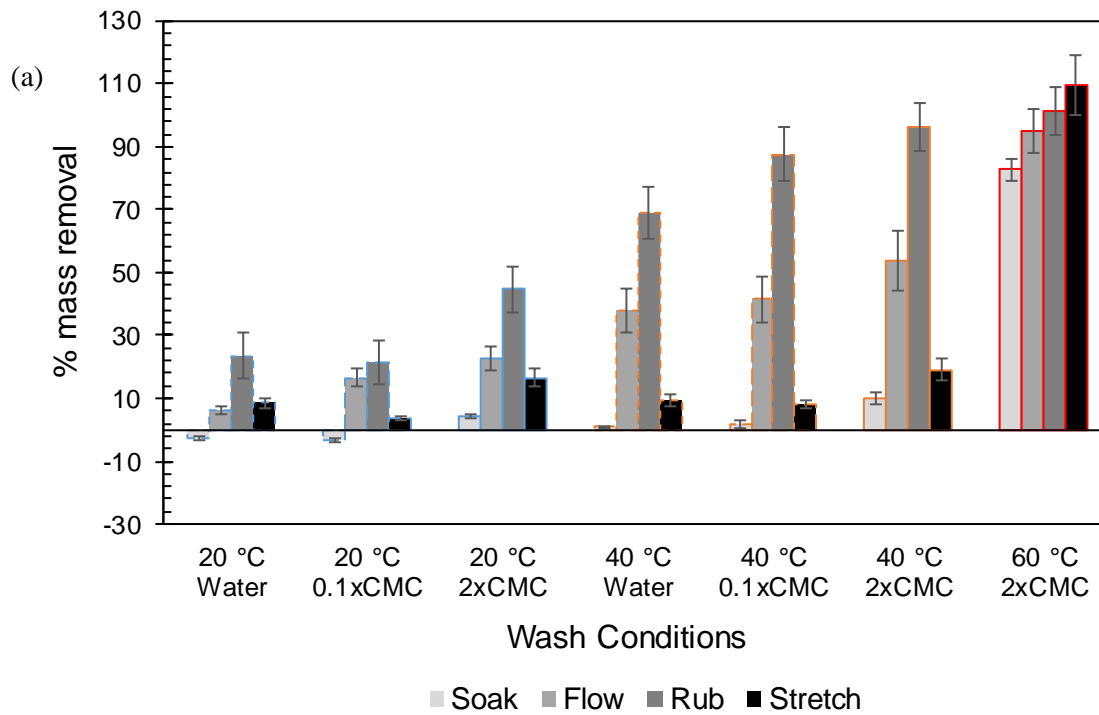
8.2. Cotton

Figure 8.2 presents the removal of sebum from cotton by soaking, flow, rubbing and stretching. As with polyester, overall removal of sebum from cotton is highest when rubbing is used compared to soaking, stretching and flow. For cotton, the range of removal as measured by mass when the fabric is rubbed is between 23.5 and 101.3 %. Removal of over 100 % suggests some fabric fibres may also have been lost during rubbing. The increase in L^* and decrease in a^* show the most improvement when rubbing is used, with ranges of 23.2 to 88.0 % and 25.1 to 85.1 % respectively. The decrease in resistance is also greatest for rubbing under most wash conditions, ranging from 39.0 to 99.9 %.

Unlike polyester, removal of sebum from cotton is lowest when soaking alone is used under all conditions using all measures of cleaning. Interestingly, at 60 °C with twice the CMC of the surfactant, mass removal is 82 %, which is much higher than the 32 % observed for polyester. This is thought to be due to the accessibility of the sebum on the cotton surface, whereas on polyester the sebum is embedded within the fabric. Cotton also contains significantly less sebum than polyester, $9.687 \pm 0.49 \text{ mg.cm}^{-2}$ compared to $32.30 \pm 1.61 \text{ mg.cm}^{-2}$ on polyester, which is likely to affect removal. For mass removal, the fabric is found to have increased in mass when it has been soaked at 20 °C with low concentration of surfactant or water. This is likely to be due to absorption of water by the sebum. At all other temperatures, removal is below 10.1 % mass loss. This shows that chemical action alone is not sufficient for maximum removal, and is most effective when used in conjunction with other actions. The effect observed above for polyester stretched at 40 °C with surfactant is not observed for cotton. This may be due to the more regular nature of the cotton weave, compared to the varied pore sizes observed with knitted polyester.

Removal by flow of wash solution is greater than stretching for cotton under most conditions. At 20 and 40 °C, the range of removal for flow is 6.3 to 53.7 %, compared to 3.8 to 19.0 % for stretching. This is likely to be because the shear force of the flow of wash solution is able to remove more sebum trapped in the crevices of the fibres on the cotton surface. Stretching is not able to remove this soil,

and is likely to further trap it within these crevices. For polyester, the fibres are smooth so the same effect is not observed. The exception to this is when 60 °C wash solution is used, where removal by stretching is 109.7 % compared to 95.3 % for flow. It is likely that this is due to loss of fibres from the fabric that has been stretched, supported by the fact that the improvement in colour is not so drastic. For stretching, the improvement in L* and a* range from 5.4 to 66.5 %. The improvement for flow is greater, ranging from 6.4 to 88.0 %. As with polyester, flow is the best action for removing sebum from the pores of the fabric and hence displays a greater decrease in resistance. The range of improvement for flow is 36.3 to 100 %, compared to stretching, where decrease in resistance ranges from 11.4 to 99.9 %. When the highest temperature is discounted the improvements for flow and stretching decrease to 91.0 % and 39.1 %, respectively.



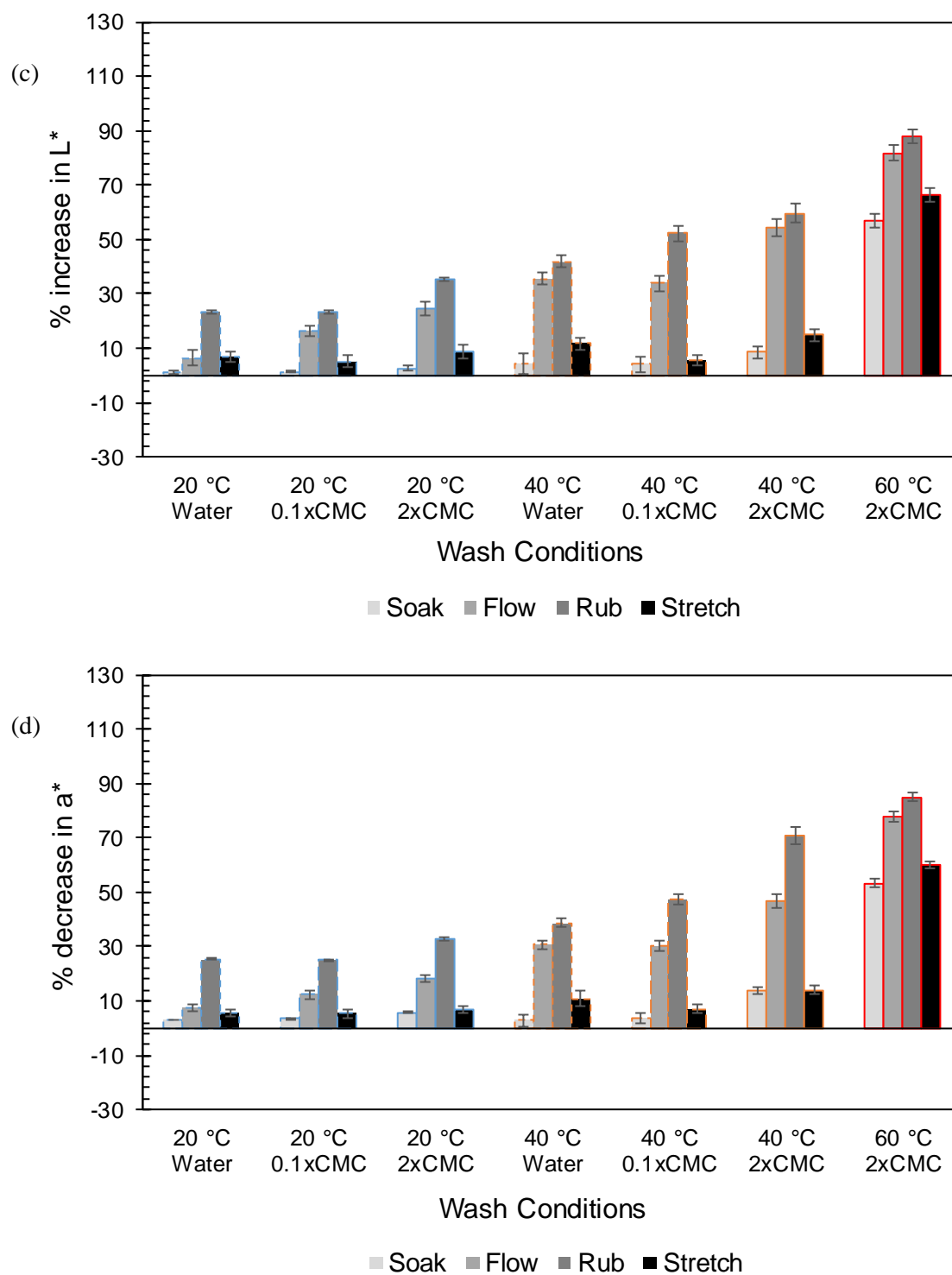


Figure 8.2. Comparing the effect of chemical action, hydrodynamics and mechanical actions on cotton soiled with sebum. Cleaning is measured by (a) % mass removal, (b) % decrease in resistance, (c) % increase in L^* and (d) % decrease in a^* . The error bars represent \pm one standard deviation for three fabrics. Five measurements were taken from each fabric for colour and resistance.

Chapter 9: Conclusions and Future Work

9.1. Conclusion

Virgin and soiled polyester and cotton fabrics have been characterised using SEM, FTIR, zeta potential, contact angle and yarn, fibre and pore size measurements. The difference in the fabric fibres have been observed, as well as the knit pattern used for polyester and weave pattern of the cotton fabric. Sebum has also been analysed using FTIR, SEM and DSC.

Removal of sebum from cotton and polyester fabrics has been investigated using a model single surfactant system at a 20 °C, 40 °C and 60 °C. The surfactant has been used at 0.1 and two times its CMC, and compared to water. Bespoke equipment has been used to separate the effects of chemical action, hydrodynamics and mechanical actions of rubbing and stretching. A number of analysis methods have been used to understand removal mechanisms.

Both improvements to the equipment and methods have been implemented to give more reliable and representative results. This includes design and production of a new rubbing rig which allows the full length of the fabric to be tested. Tensioning rollers have been added to the stretching and rubbing rigs, and heat exchange tubes have been added to all rigs to enable consistent temperature throughout the duration of experiments. An updated flow chamber has been produced speeding up change over time between experiments.

Cleaning has been characterised by mass removal, decrease in resistance and colour change. All values have been given as percentage changes to allow comparison between different measures of cleaning. Mass removal gives an indication of the total amount of mass of soil that has been removed from the fabric. Resistance is primarily effected by the amount of sebum in the pores of the fabric, therefore a decrease in resistance gives information about interpore removal. For colour change, the increase in L* (lightness) and decrease in a* (redness) have been reported. Additionally, FTIR, mass

per unit area and the colour of the top and under side of the fabric have been investigated for all fabrics, and SEM and zeta potential have been found for a number of cleaning conditions.

For all cleaning actions, removal was found to be highest with 60 °C wash solution containing surfactant at twice the CMC. This is to be expected as 60 °C is significantly above the melting point of sebum, and LAS is known to effectively remove oily soils when used at higher concentrations. Generally, removal was higher at 40 °C than 20 °C, and increased surfactant concentration aided removal, however some exceptions to this were found.

Flow regimes were investigated to establish the optimum conditions. For both fabrics, removal was highest using through flow at 6 L.min⁻¹. Interestingly, when cross flow was used on polyester the lower flow rate, 3 L.min⁻¹, increased removal compared to the higher flow rate. It is suspected that this is due to the increased shear force of the higher flow rate pushing sebum further in to the pores of the fabric. When temperature and surfactant concentration were investigated removal was found to increase with increases in both of these conditions.

Fluid Dynamic Gauging, a novel technique for investigation of fabrics, was used to test the strength of sebum soil on fabric. FDG was found to pull sebum through the pores of the fabric, removing the majority of the sebum from the underside and depositing additional sebum on the top surface. This effect was found to be proportional to the amount of shear stress applied by the gauge. There is scope for further development of FDG as a technique to investigate fabric soiling and cleaning, but an improved method of tensioning the fabric is required. Of interest would be the effect of the gauge on the fabric when the fabric is not supported by a metal plate, as it has been in these experiments.

When rubbing action was used on polyester a similar increase in the level of cleaning was observed for each temperature, however, for cotton, a much higher increase in removal of sebum was observed at 40 °C than at other temperatures. This suggests a synergistic effect between temperature and rubbing action. A similar increase was not observed at 60 °C, which is likely to be due to the fact

that cleaning was already high at this temperature, with much less room for improvement. It was also found that surfactant aided removal of sebum with rubbing, even at low concentration. This suggests that the surfactant loosens the soil making it more easily removed by the rubbing blade.

When polyester was cleaned using the stretching rig, removal was negligible at 40 °C, and on some measures of cleanliness the fabric appeared to be less clean than the soiled fabric. It is suspected that the solubilised sebum had become trapped in the pores of the fabric due to the complex structure of the elasticated knit. The same effect was not observed with the more regular weaved cotton.

Overall, of the four actions used to investigate cleaning, rubbing was the most effective for both fabrics, and chemical action was the least effective. Stretching and flow were both somewhat effective, and the most effective depended on the temperature and surfactant concentration used.

9.2. Future Work

9.2.1. Expansion of current work

Different combinations of fabrics, soils and chemicals could be tested including polyester and cotton fabrics with both oily and particulate soils. It is well known that different soils adhere to surfaces with vastly different strengths of adhesion. This will allow investigation into whether the biggest differences between results are found to be due to soil or due to fabric.

9.2.1.1. Fabrics

Current work has focused mainly on 100% knitted polyester and 100% woven cotton. It would be interesting to explore other fabrics including blended fabrics and different fabric thicknesses. Polycotton is becoming a more popular fabric choice for clothing as it combines the benefits of both polyester and cotton, therefore may be more relevant for future testing. It would also be interesting to test a woven polyester or a knitted cotton to investigate whether differences are due to fabric type or the structure of the fabric.

9.2.1.2. Stains

It is known that oily soils aid the adhesion of particulate soils to the surface of the fabric. It would be interesting to test a particulate soil such as carbon black both without and in combination with oily soil. This would allow investigation into possible adhesive interactions between particulate and oily soils that may inhibit soil removal.

9.2.1.3. Chemicals

Current work has focused on a single surfactant system, and although this surfactant is a major component in laundry detergent, it would be interesting to expand the testing to other single surfactants currently used in laundry detergent, as well as exploring mixtures of surfactants. It would also be interesting to investigate other components of laundry detergents such as enzymes. Enzymes target specific stains and are known to increase cleaning at lower temperatures, therefore investigation of this could lead to promising results.

9.2.2. Exploration of new technologies

The impact of using ultrasound, gas sparging or micro bubbles could be investigated to identify potential methods for enhancement of low temperature cleaning. These technologies may be able to compensate for the loss of thermal energy, in particular when combined with flow or mechanical action.

9.2.3. Investigation of water hardness

It has been found that detergency decreases significantly as water hardness is increased, therefore the same would be expected of this surfactant systems. The decrease in detergency is more dramatic for anionic surfactant systems, and therefore the results would be more applicable to the consumer. This could be investigated by adding magnesium chloride to the wash solution and repeating a number of key results from the experiments already performed.

9.2.4. Development of new equipment

9.2.4.1. Compression

It has been noticed in experiments that clamping fabrics in the stretching and rubbing rigs leads to some removal of soil on the surface. In practice, particularly in a washing machine, fabrics will be compressed by the rest of the wash load against the side of the drum during the wash cycle. It is also likely that fabrics are compressed during hand washing, either in the consumers hand or beaten against a surface such as a rock. A further development of this project could involve the design and building of a rig to simulate compression. The rig could be designed to allow compression against a solid metal surface or against a number of stacked pieces of fabric.

9.2.4.2. Twisting

Another action likely to occur during washing is twisting. This has been considered during this project, but it was decided due to financial and time constraints that this should not be a priority. During discussions it was also raising that this testing would be difficult as it would be impossible to apply the same force consistently along the length of the test fabric. It has been speculated that twisting occurs during the rinsing of fabrics when hand washing, at the point when the consumer is already satisfied that the fabric is clean. However in a washing machine twisting is likely to occur throughout the wash cycle. It may be worth revisiting in the future if the issue of a consistent force along the length of the fabric during twisting can be addressed.

9.2.5. Single Fibre

The cleaning of an individual fibre would also be an interesting area to investigate. The results from this could be compared to results from the whole piece of fabric, and would give some idea of the effect of the structure of the fabric on the overall cleaning. It is suspected that the pores of the fabric have a large role in the cleaning.

9.2.6. Investigation of soaking

Although fabrics have been soaked during equipment set up, it would be interesting to investigate the effect of soaking them for longer prior to testing. Soaking could be done in water or surfactant solution to loosen the soil. An interesting set of experiments could involve soaking the fabric in hotter water then cleaning using flow and mechanical action at a lower temperature. This may lead to an overall lowering of energy used while still benefiting from the removal seen using high temperatures.

9.2.7. Development of FDG

9.2.7.1. FDG during flow experiments

Some initial testing was completed with the FDG set up on the Flow Rig however it is difficult to keep the fabric sufficiently taut during experiments. Even when a solid plate was placed under the fabric results were variable and often didn't produce the characteristic curve expected from FDG experiments. If a suitable way to tension the fabric could be incorporated in to the experimental set up this would give interesting analysis of the shear stress required to remove the deposit during flow experiments.

9.2.7.2. Vertical equipment set up

During discussions at an FDG workshop regarding the difficulties of gauging with fabrics, in particular the difficulties encountered when trying to stretch the fabric to avoid movement towards the gauge as it approaches the surface, it was suggested that the fabric could be hung vertically with a weight attached to this. The gauge would then also be mounted perpendicular to the fabric surface; a set up used by Gu et al (2011). During discussions it was also suggested that rather than having one gauge, two gauging tubes could be used on either side of the fabric. This would avoid the issues of the fabric being pulled towards one gauging tube, however there are a few issues with this suggestion. Firstly, the two gauging tubes would need to be perfectly aligned, and secondly the pressure from each

tube would need to be exactly identical. Another disadvantage of using this approach would be that the interesting results found when the gauge pulls the soil through the fabric would not be seen. It may still be something to consider investigating in future projects.

9.2.8. Rubbing against another fabric

The blade on the rubbing rig is designed to also accommodate a piece of fabric to provide a fabric-on-fabric rub. It would be interesting to investigate this, and to investigate whether the direction of fibres when the fabric is attached has an effect on cleaning.

9.2.9. Combinations of mechanical actions and hydrodynamics

It would be interesting to investigate the effect of rubbing, stretching and hydrodynamics when used sequentially. For example, stretching alone has not provided effective cleaning, but perhaps may loosen soil sufficiently to allow more effective rubbing. The order in which the rigs are used is also likely to have an effect and therefore experiments should include different combinations used in different orders.

9.2.10. Comparison to conventional washing methods

Fabrics could be washed in a washing machine or by hand under the same conditions as the fabrics studied in this thesis for comparison. This would give a better indication of whether the forces used in these experiments were of the correct magnitude. Difficulties would arise when trying to control hand washing to give a consistent wash across all conditions.

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Chapter 11: Appendix

List of Appendices

A. Fabric Resistance Tests

B. Error Calculation

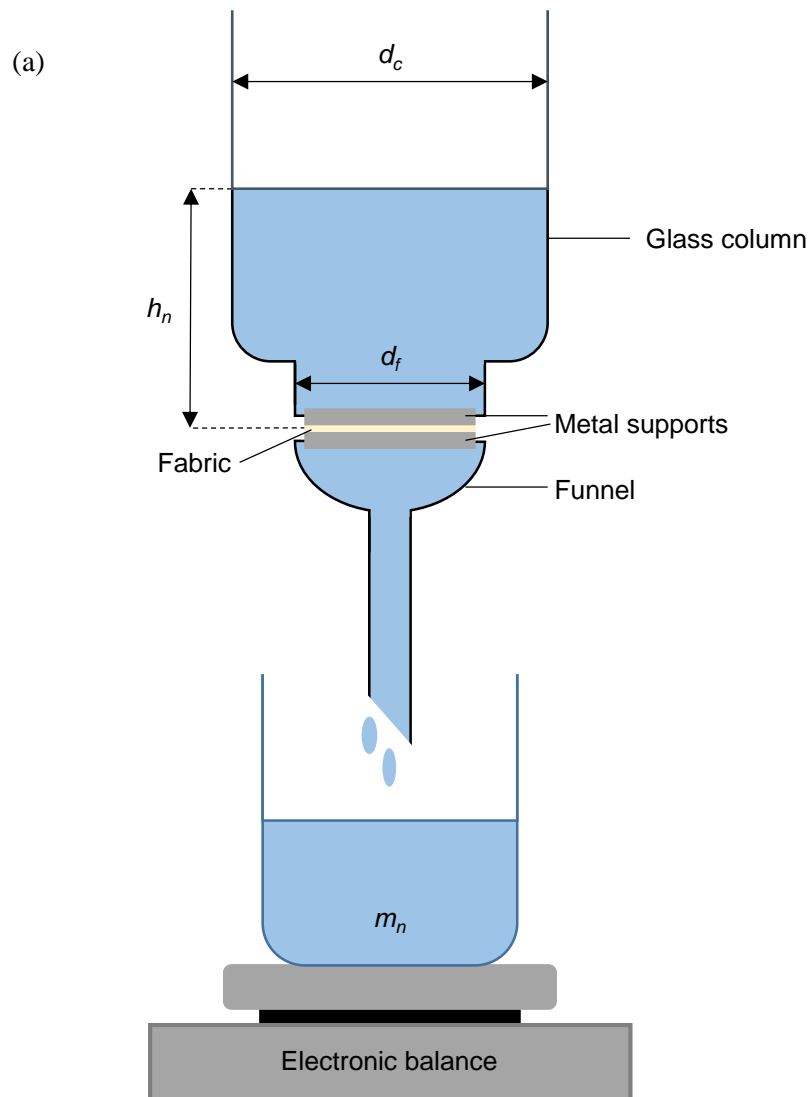
C. Mechanical Drawings

A. Fabric Resistance Tests

The flow through the apparatus shown in Figure A1 can be described by Darcy's Law:

$$\Delta p = \frac{\mu u l}{K}$$

The equipment was assembled to measure resistances of fabrics using Darcy's Law, a similar method to that employed by Lewis (2015).



(b)

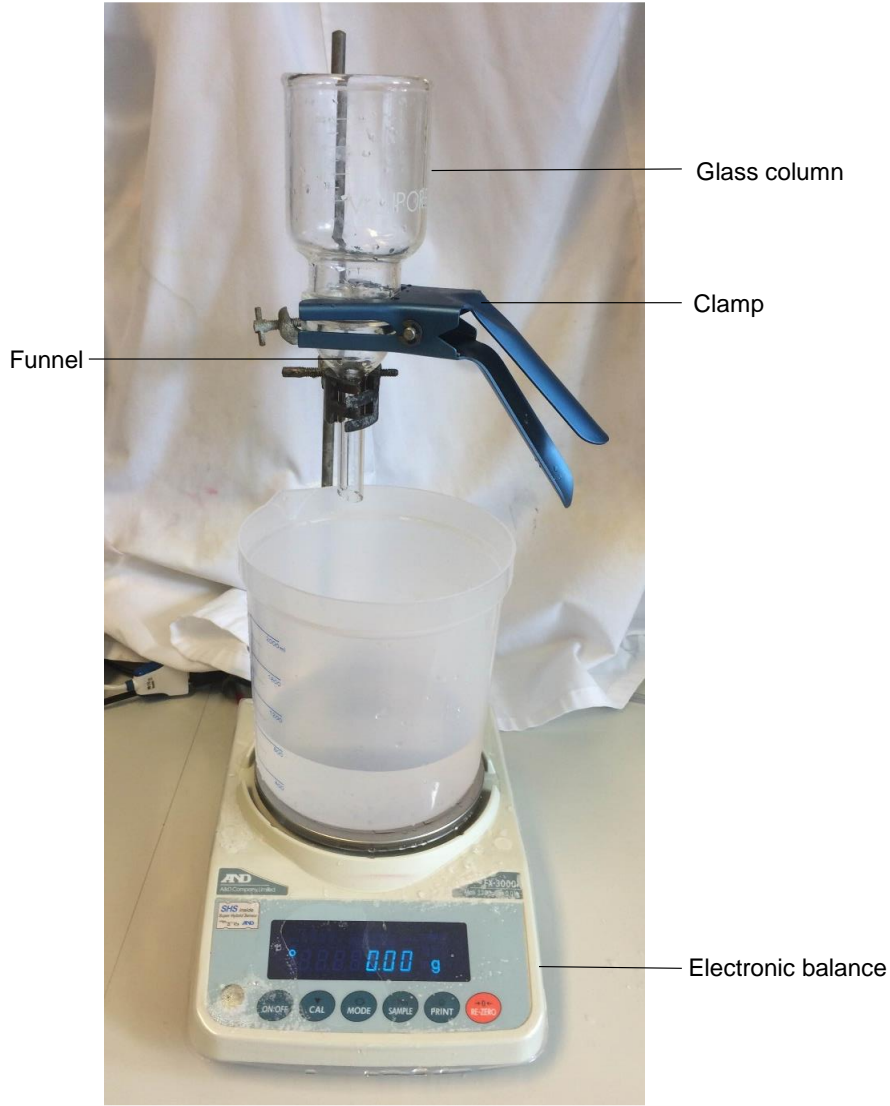


Figure A1. (a) Schematic diagram and (b) image of experimental set up for measuring resistance of fabrics

The mass of RO water flowing through the fabric sample over a given time period was measured on an electronic balance connected to a data-logging PC. Mass measurements were then converted to height measurements, and Darcy's Law rearranged to allow calculation of R_m , as shown below.

$$u = -\left(\frac{d_c^2}{d_f^2}\right) \frac{dh}{dt} = \frac{\Delta p K}{\mu l} = \frac{\Delta p}{\mu R_m} = \frac{\rho g h}{\mu R_m}$$

Equation 1

This can be integrated to give:

$$-\int_{h_0}^{h_n} \frac{1}{h} dh = \left(\frac{d_f^2}{d_c^2} \right) \frac{\rho g}{\mu R_m} \int_{t_0}^{t_n} dt$$

Equation 2

$$-[\ln h]_{h_0}^{h_n} = \left(\frac{d_f^2}{d_c^2} \right) \frac{\rho g}{\mu R_m} [t_n - t_0]$$

Equation 3

Since $t_0 = 0$:

$$\ln[h_n] = \ln[h_0] - \left(\frac{d_f^2}{d_c^2} \right) \frac{\rho g}{\mu R_m} t_n$$

Equation 4

It not possible to measure h_n therefore mass is measured and convert to height using Equation 5 below.

$$h_n = h_0 - \frac{m_n - m_0}{\rho} \frac{4}{\pi d_c^2}$$

Equation 5

$$\ln \left[h_0 - \frac{m_n - m_0}{\rho} \frac{4}{\pi d_c^2} \right] = \ln[h_0] - \left(\frac{d_f^2}{d_c^2} \right) \frac{\rho g}{\mu R_m} t_n$$

Equation 6

Equation 6 is then plotted and the inverse of the slope used to give R_m .

B. Initial Analysis Method

Mass measurements obtained using method 1 in 3.5.1.1, where area was also measured and the sample was heated, produced results with large error bars as shown in Figure B1. For this reason an alternative method of measuring mass was used.

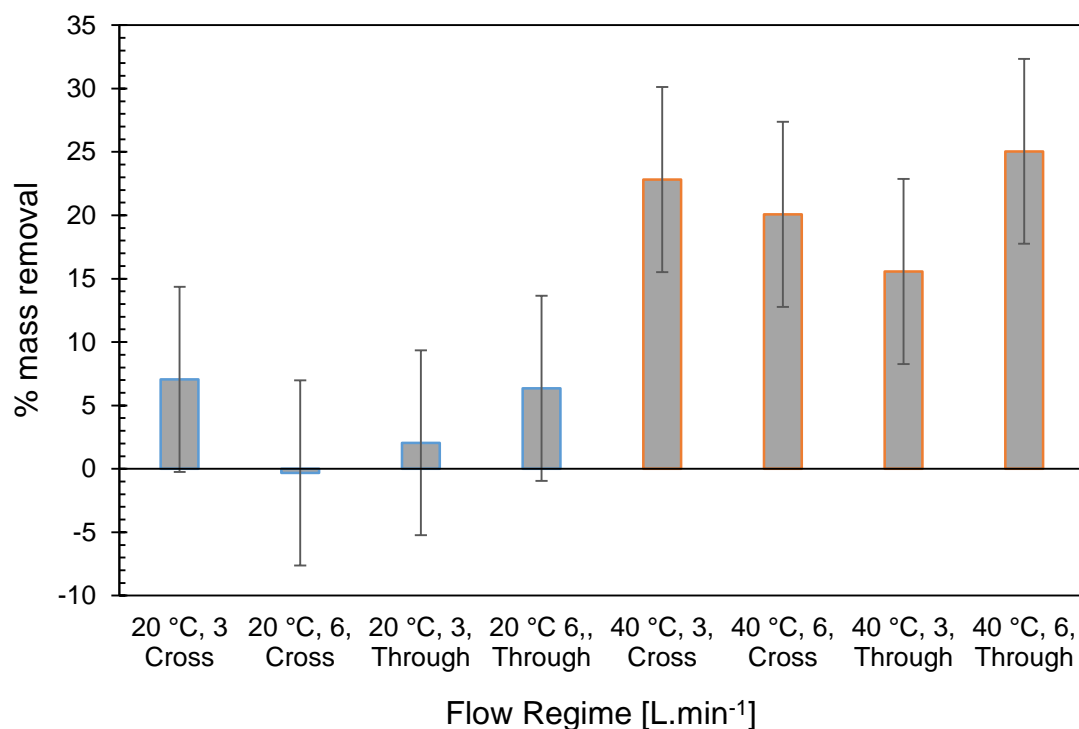


Figure B1. Flow experiment at 20 °C and 40 °C with cross and through flow at 3 and 6 L.min⁻¹. 3 repeat tests were performed on polycotton fabric fouled using method 1.

C. Mechanical Drawings

C.1. Flow Rig

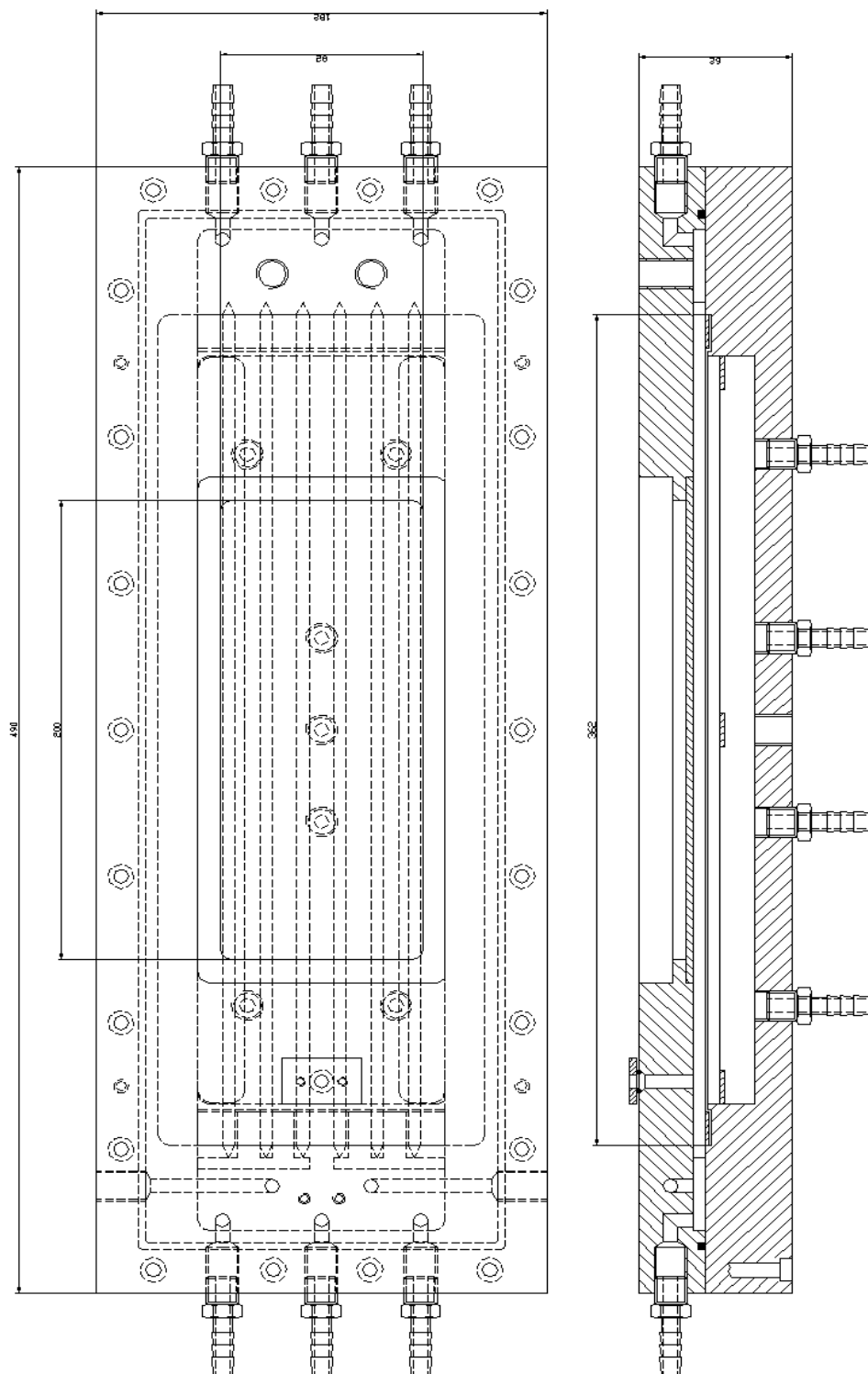


Figure C1. Mechanical drawing of flow rig

C.2. Stretching Rig

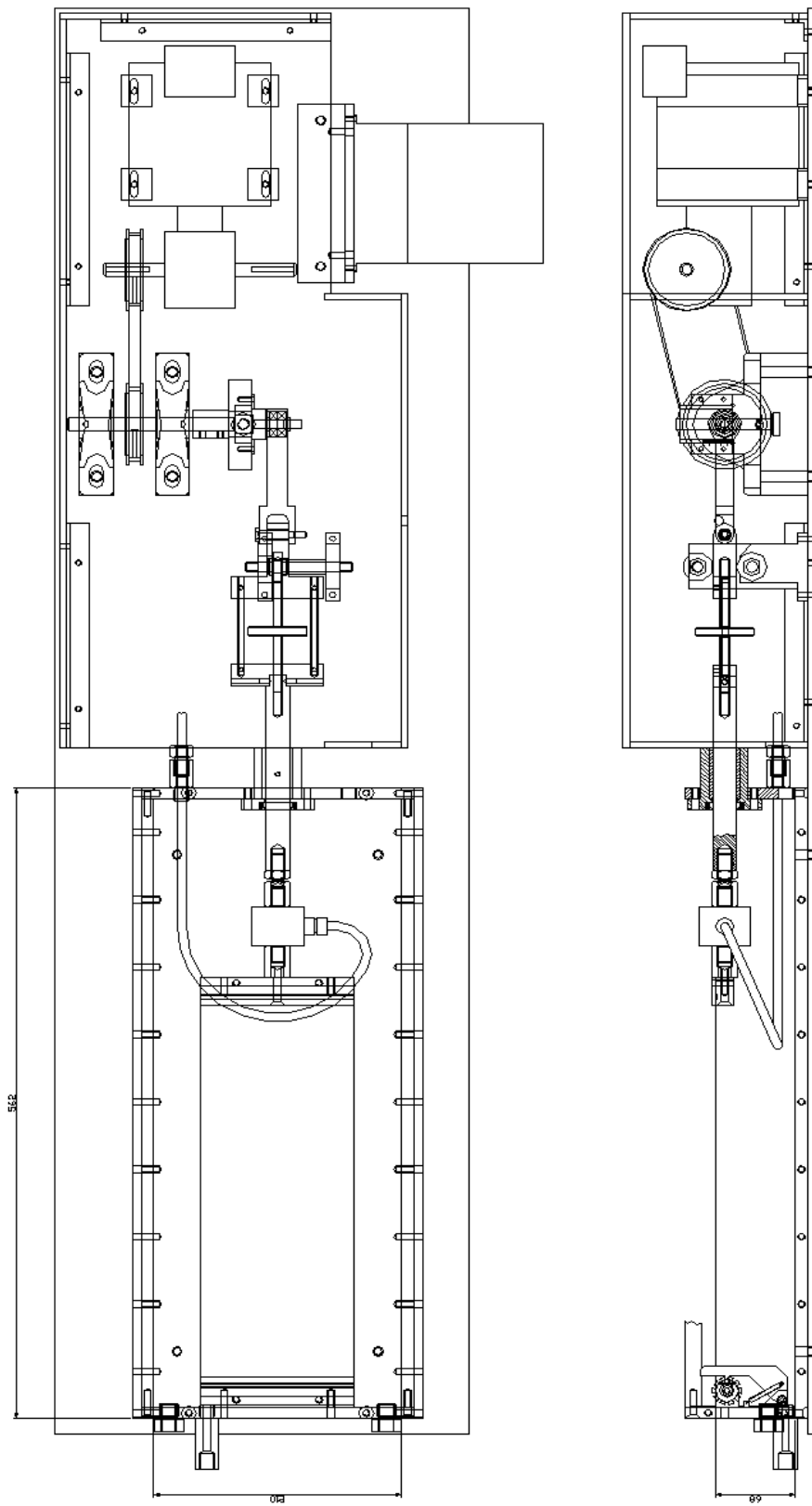


Figure C2. Mechanical drawing of stretching rig.

C.3. Tensioning Wheel

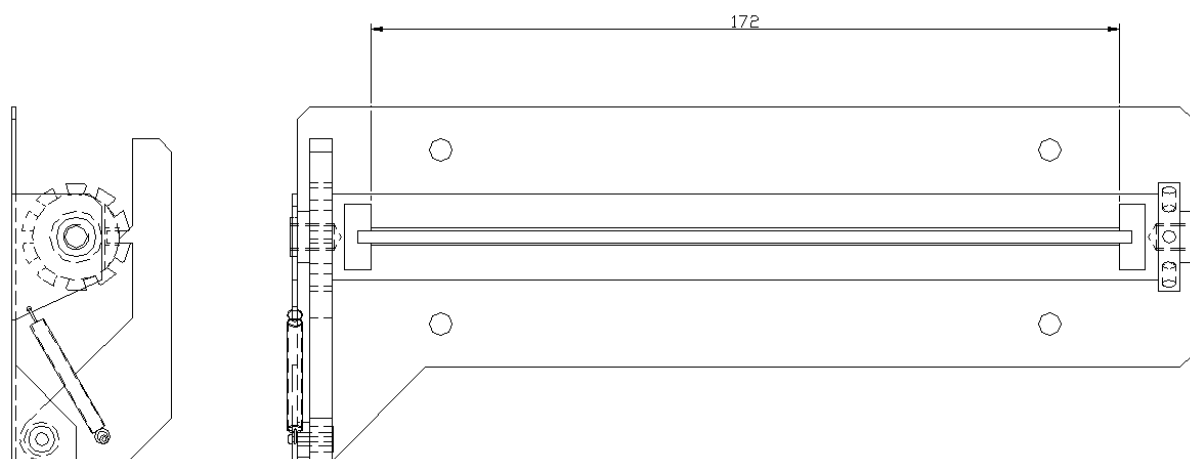


Figure C3. Mechanical drawing of tensioning wheel used in rubbing rig and stretching rig.

C.4. Rubbing Rig

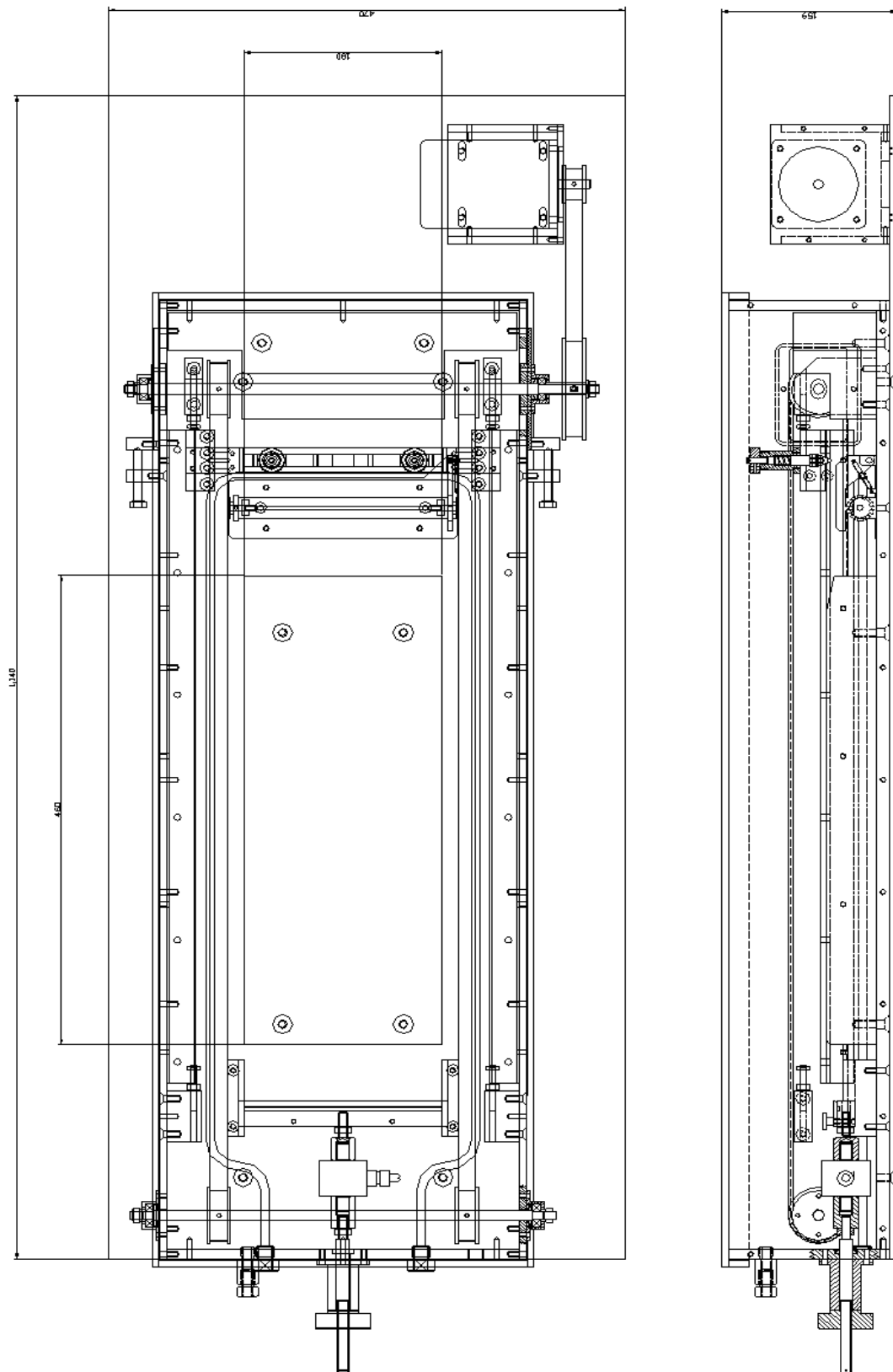


Figure C4. Mechanical drawing of rubbing rig